

**A PROVISIONAL ASSESSMENT OF RISK ASSOCIATED  
WITH HEAVY METAL ACCUMULATION IN NEW  
ZEALAND AGRICULTURAL SOIL**

*Effects of landfarming and fertiliser use on the heavy metal  
concentration in plants*

A thesis presented in partial fulfilment of the requirements for the degree of

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## Abstract

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This study investigated heavy metal accumulation in New Zealand agricultural soil (horticultural soil and landfarm-impacted soil), factors influencing their concentration in leafy vegetables and pasture, and the potential implications to food safety, animal welfare and human welfare. The study also sought to verify the hypothesis that “landfarming poses no threat to pasture and animal welfare” with respect to heavy metal accumulation. In addition, hemp phytoremediation potential was also explored for landfarm-impacted soil.

This study is a synthesis of two glasshouse trials that have, as a common denominator, heavy metal accumulation in New Zealand agricultural soil. The first project assessed cadmium accumulation in leafy vegetables (spinach, silverbeet and lettuce) grown on two New Zealand commercial horticultural soils while the second project focused on heavy metal accumulation in pasture (ryegrass) and a cash crop (hemp) grown on agricultural soil that had been amended with drilling waste. Bulk composite soil samples used for this glasshouse trial were collected from commercial horticultural farms in two locations (Pukekohe and Gisborne), while a landfarm-impacted soil and drilling waste from oil exploration and production sites was collected from the Taranaki region. Soil samples were crushed and potted into replicate pots containing (4kg). Lettuce, spinach and silverbeet were seeded in horticultural soils while ryegrass and hemp were seeded in impacted soils. All soil and plant samples were harvested and taken to the Soil and Earth Science laboratory, Massey University Palmerston North for analysis of heavy metal concentration (Cd, Zn, Cu and Ni) and dehydrogenase activity. Descriptive statistics and ANOVA of means was conducted using Minitab 17.

The total Cd concentration in the Pukekohe soil was 0.26 mg Cd/kg soil and that in the Gisborne soil 0.11 mg Cd/kg. The Cd, Cu, Ni and Zn concentration in the landfarm-impacted soil was 0.1 mg Cd/kg; 12.57 mg Cu/kg; below detection limit (BDL) for Ni and 29.99 mg Zn/kg respectively. These values were not significantly different to concentrations in an adjacent control soil collected at the same time for the pot experiment (0.1 mg Cd/kg, 11.5 mg Cu/kg, 29.14 mg Zn/kg, and Ni (BDL)). The Cd concentration in all leafy vegetables grown on the horticultural soil and sampled at two time points (spinach, silverbeet and lettuce) exceeded tolerable limits for Cd in agronomic crops (0.05 - 0.5 mg Cd/kg) with the exception of lettuce (in Pukekohe and Gisborne soil at final stage) and silverbeet (in Pukekohe soil at final stage). Spinach showed elevated Cd accumulation (0.27 mg/kg FW) above CODEX (2010) and FSANZ (2011) limits for the Gisborne soil. The heavy metal concentration (Cd, Zn, Ni and Cu) in hemp and ryegrass grown on the landfarm-impacted soil and control were not significantly different but within tolerable limits in agronomic crops (Cu: 5 – 20 mg/kg; Zn: 50 – 100 mg/kg; Ni: 1- 10 mg/kg). Soil pH is the dominant factor influencing metal bioavailability while organic matter content, and oxalate extractable Al and Fe oxide content (sesquioxides) also affects cadmium bioavailability in agricultural soils.

There was no evidence of a heavy metal (Zn, Ni, Cu and Cd) concentration above soil limits defined for the safe application of biosolids in horticultural and landfarm-impacted soils. This suggests that animal wellbeing (via soil ingestion) and food safety will not be affected as a result of land application of drilling waste and long history of P fertiliser use. However, cadmium and heavy metal management is necessary to prevent elevated accumulation over time. Elevated Cd concentration in spinach does not pose direct threat to human consumers but has the potential to limit the accessibility of this product in export markets.

A soil heavy metal concentration below biosolids guidelines in the landfarm-impacted soil implies that remediation of this land is not necessary. This observation was supported by data on soil microbial activity in the landfarm-impacted soil which showed no difference from the control soil. The data does not support the public perception and industry concerns that heavy metal accumulation in landfarm-impacted soil poses a health risk. In case of a continued halt in milk collection from landfarm-impacted sites by the dairy industries, a cash crop (hemp) with no exposure pathway and high biomass quality (under landfarm-impacted soil) that potentially has high economic value could replace the traditionally ryegrass system, changing the agricultural land use from a food one to a non-food one.

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## Chapter 1 : Introduction

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Heavy metals are metallic and semi-metallic (metalloids) chemical elements of high density ( $> 5 \text{ g/cm}^3$ ) with most of them toxic and carcinogenic even at low concentrations. Widely known heavy metals are mercury, cadmium, arsenic and chromium (Dinis & Fiuza, 2010). Heavy metals are naturally occurring elements in the soil environment due to pedogenic process of rock weathering, and are generally present at trace levels ( $<1000 \text{ mg/kg}$ ) (Kabata-Pendias & Pendias, 2001; Wuana & Okieimen, 2011). Some heavy metals are essential to microbial functions in soil at an acceptable levels and conversely at toxic levels (Jeyakumar et al., 2010). There is a rising concern globally of the implications of soil contamination from a variety of potential pollutants involving heavy metals (Gray & McLaren, 2006). Heavy metal accumulation in soil is of concern in many countries due to the impact this can have on food quality and soil health (Gray & McLaren, 2006). In New Zealand, heavy metals, especially cadmium, have been associated with potential threats to human health, trade and land use flexibility (MAF, 2011).

Heavy metal accumulation in agricultural soil is facilitated by anthropogenic activities involving emissions from industrial activities, fertiliser application, sewage disposal, animal dung, pesticides, coal combustion, petrochemical spillage and atmospheric combustion (Wuana & Okieimen, 2011). A typical example in New Zealand is the antecedent use of hazardous chemicals in industry, agriculture and horticulture that has left an imprint of soil contamination (MfE, 2010). Past activities that have resulted in soil contamination in New Zealand include; pesticide production/use, gas and coal mining, petroleum exploration and storage, timber treatments and sheep dipping (MfE, 2010).

The distinction between contamination and pollution has been provided by Chapman (2007). Contamination can only occur when the concentration of substance is above regulatory background level while pollution is a contamination that leads to threatening biological effects to the inhabitant community (Chapman, 2007). It is therefore important to note that all pollutants are contaminants but not all contaminants are pollutants (Chapman, 2007). This differentiation is generally determined by the substance bioavailability to relevant organisms which may be facilitated by their chemical form, changing factors in the environment, the environmental subdivision they occupy and the reactions (behavioural and physiological) of the endangered biota (Chapman et al., 2003). Soil contamination becomes a threat to the environment when the concentration of hazardous substance in a particular location has a likely chance of leading to an adverse effect on human health and the environment (MfE, 2010; Jeyakumar et al., 2008). Assessing when contamination may become pollution demands a weight of evidence (WOE) evaluation using diverse line of evidence (LOE) that matches the scenario under investigation (Chapman, 2007). A WOE assessment involves a comprehensive study of the ecological risk assessment associated with the contaminant (Chapman, 2007). Information on the exposure pathways to stressors and the implications of those exposures is required for the ecological risk assessment of contaminants (Chapman, 2007). Primary and secondary receptors are of major concern in a contaminated risk assessment (Chapman, 2007). Primary receptor species are the organisms (plants, microorganism etc) resident or expected to inhabit a contaminated site while secondary receptors species (humans, animals etc) are the consumers of the primary receptor species (Chapman, 2007). The potential risk of contamination is greater in an environment used for food production or one in close relation to residential areas, people, water bodies and essential habitats (MfE, 2010). Two important

contaminants of concern in New Zealand environment are cadmium and fluorine due to their presence as incidental impurities in phosphate rocks utilised for fertiliser production and their threat to economy and trade in New Zealand (McLaren, 2007; Loganathan et al., 2003). Phosphorus fertilisers also contain other impurities such as arsenic, chromium, strontium, uranium and zinc (Loganathan et al., 2003). Other sources of agriculture-related heavy metals in New Zealand are the land application of biosolids (i.e. copper, zinc, lead, cadmium, nickel, and chromium), livestock dung (arsenic, zinc), agrochemicals (lead, zinc, lead, arsenic) and atmospheric deposition (copper, zinc, cadmium, nickel, lead and chromium) (McLaren, 2007).

Soil quality guidelines exist for the protection of human health and the environment from heavy metal contamination (Cavanagh, 2006a). The soil quality guideline for a safe application of biosolids gives a national guidance for the application of biosolids to agricultural land (NZWWA, 2003) and provides a framework for biosolids management in New Zealand (NZWWA, 2003). The guideline was produced by a joint committee formed by the New Zealand Water and Waste Association, representing major stakeholders that included wastewater industry, user groups, central and local government and environmental groups (NZWWA, 2003). The soil quality guidelines are designed to support biosolids management in New Zealand for the minimisation of adverse effects on human health (from metal contamination), the environment and the economy (NZWWA, 2003). It is specifically designed to: safeguard the life-supporting capacity of soils, promote the responsible use of biosolids, protect public health and the environment, identify the risks (plant health, animal health and soil microbial processes) associated with biosolids use and minimise risks to the economy (NZWWA, 2003). Biosolids guidelines set a maximum soil limit to which biosolids-derived heavy metal concentrations (arsenic, cadmium, zinc, chromium, copper, lead, mercury, and nickel)

in soil can increase (NZWWA, 2003), and these limits have been adopted by many commentators as an unofficial threshold level for soil contamination (e.g for extractable (bioavailable) cadmium the concentration limit is 1 mg/kg). However, regulatory soil limits for heavy metals are defined by the National Environmental Standards (MfE, 2010).

Formal limits for maximum concentration in soil (e.g the NES) are relevant to agricultural land use because they are one of the uptake parameter that represents total heavy metal concentration. However, extractable levels (bioavailable levels) are more important in the agricultural setting. To manage the specific issue of cadmium in agricultural soil, a government and private sector partnership called “The National Cadmium Management Strategy” administered by a Cadmium Management Group manages cadmium accumulation in New Zealand agricultural soils to minimise risk to human health and the environment on a long term basis (of at least 100 years, FANZ, 2014). The Cadmium Management Group comprises of the following stakeholders; Ministry of Primary Industry (MPI), agricultural sector groups (involving Federated farmers, Beef and Lamb New Zealand, delegates from; Dairy industry, Arable Food Industry, Horticulture New Zealand and Fertilizer industry) and Regional Councils (FANZ, 2014). The Group initiated the Tiered Fertiliser Management System (TFMS) for soil cadmium management with trigger values (total) derived from national soil quality guideline documents for cadmium management in New Zealand agricultural soils (MAF, 2011; MPI, 2012).

### **1.1. Problem Statement**

New Zealand’s primary production sector depends on fertiliser to sustain high rates of production, and phosphate fertilizer sourced from phosphate rocks is a key nutrient

input. Cadmium is a soil contaminant that is naturally present in phosphate fertiliser and this element has built up in soil with time. The implication of soil cadmium concentration on economically important cultivars of leafy green vegetables, pasture, and forage crops etc. in New Zealand is poorly understood. Limited data is available on factors influencing increasing cadmium uptake by different plant species and its accumulation in soil with high rates and long history of phosphate fertiliser use. Based on these knowledge gaps, the Ministry for Primary Industry has recommended that research studies determine the influence of plant species, cultivars and soil properties on cadmium uptake from New Zealand agricultural soil with high rates and long history of phosphate fertiliser use (MPI, 2012). MPI's recommendation is aimed at developing a specific risk-based soil guideline for the protection of four relevant endpoints (human health, ecological receptors, food standard and groundwater). Site-specific risk-based soil guidelines will support review and development of MPI's Tiered Fertiliser Management System (TFMS) by the Cadmium Working Group. Among these endpoints, protection of food standards and ecological receptors from cadmium contamination has been identified as the most relevant to New Zealand agricultural land. Developing specific risk-based guidelines necessitates an analysis of metal pathways and an assessment of its effects on a particular organism (plants etc) (NZWWA, 2003). It also involves analysis of metal balance through consideration of rates of removal by crop, soil erosion and leaching etc (NZWWA, 2003). Current work demonstrates a principle of maintaining soil metal concentration below background levels to avoid any potential risk to the environment (NZWWA, 2003).

Research on heavy metals in New Zealand is largely focused on cadmium. Considerably less data exist for the assessment of threats posed by other metals (nickel, chromium, cobalt, zinc, copper, uranium, mercury) in New Zealand agricultural soil.

There are other sources of heavy metal contaminants that affect productive land. For example, the land application of drilling waste from oil and gas exploration wells is a rising concern in New Zealand. Although Cavanagh (2015) in an MPI commissioned report described that there was an absence of evidence for potential environmental threats from heavy metals in landfarm-impacted sites, there remains a lack of trust in the system as the public and dairy processors are concerned about the likelihood of heavy metal accumulation over time and subsequent transfer through possible exposure pathways involving pasture, meat and milk in New Zealand (Kerckhoffs et al., 2015).

There are limited studies on heavy metal accumulation in pastures and crop species grown on landfarm-impacted soil. In addition, the impact of landfarm waste on soil microbial activity is poorly understood. Microbial activity regulates organic matter and active nutrient pools (Ladd et al., 1996). This important function of microbial activity is inhibited by soil pollution with threatening impacts on crop, natural vegetation and ecosystem functioning (Ladd et al., 1996). Microbial activity is a good indicator of the extent to which contaminant is a 'pollutant' in contaminated soils (Insam et al., 1996; Kuperman & Margaret, 1997). The MPI report (Cavanagh, 2015) that aimed to assure the public and agricultural agencies of the absence of environmental threats from the disposal of oil and gas waste to agricultural soil (landfarming) welcomed critics from the public and dairy industry. Well-publicised criticisms centre on the likelihood of heavy metal accumulation overtime and subsequent transfer through possible exposure pathways involving pasture, meat and milk in New Zealand (Kerckhoffs et al., 2015). Such concerns may relate to the fact that heavy metals do not degrade in soil and build up over time due to adsorption to organic matter and the clay mineral content of soil. There is a risk that these metals may be released to food chain via plant uptake over

time (OERL<sup>1</sup>, 2011; Chibuike and Obiora, 2014). Based on the above information, more research is required to establish the actual level of contamination and risk, influencing factors and/or appropriate remediation option. It is then up to the research commissioning bodies to use the results.

The concern from dairy processors on the risks of landfarming led to the halt in milk harvest in 2014 from any landfarm sites in Taranaki region New Zealand in response to major public concerns on potential health and safety risk (Kerckhoffs et al., 2015). In response to this, major stakeholders including Taranaki Regional Council, Venture Taranaki, oil and gas explorers and affected farmers have called for a re-analysis of the risk and of alternative agricultural land use options as a way of establishing the true level of risk. Proposed in this re-analysis is the cultivation of non-food crops. This would include consideration of phytoremediation as a means of growing plants on landfarm-degraded soil with the intention of extracting heavy metals from the soil over time (Linger et al., 2002). Annual herbs with high metal accumulating potentials and little economic value are often used for phytoremediation (Linger et al., 2002). In the context of Taranaki however, industrial hemp (*Cannabis sativa*) with its high biomass and the potential economic value of harvested fibre makes this species a candidate for phytoremediation (Linger et al., 2002). Industrial hemp has therefore been chosen in this work as a promising economic and environmental option for landfarm-impacted soils due to its ability to maintain high quality fibre, high biomass under conditions of soil metal contamination (Linger et al., 2002).

## **1.2. Research aim**

The research described in this thesis was a glasshouse trial to establish heavy metal accumulation in selected New Zealand agricultural soils (horticultural soil and

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<sup>1</sup> Origin Energy Resource Limited

landfarm-impacted soil), factors influencing the accumulation of metals in leafy vegetables and pasture, and the potential implication of accumulated heavy metals to food safety, animal welfare and human welfare. The study also sought to verify the hypothesis that “*landfarming poses no threat to pasture and animal welfare*” with respect to heavy metal accumulation.

### **1.3. Objectives**

- Using glasshouse trials to establish cadmium concentration in lettuce, baby spinach (at different stages) and silverbeet grown on two New Zealand commercial horticultural soils.
- Using glasshouse trials to establish cadmium, zinc, nickel and copper concentrations in pasture (ryegrass) and cash crop (hemp) on landfarm-impacted soils.
- Assess the significance of soil properties on cadmium accumulation in the soil.
- Determine soil factors influencing cadmium, zinc, nickel and copper accumulation in leafy vegetables, ryegrass and hemp in New Zealand horticultural and impacted soils.
- Explore the phytoremediation potential of industrial hemp on landfarm-impacted soil.
- Assess the implication of landfarming on soil microbial activity; compare the heavy-metal concentration in horticultural soil and landfarm-impacted soil with risk based guidelines to determine potential risk to animal welfare, trade and food safety.

## **1.4. Importance of this research**

Understanding how plant uptake of cadmium is influenced by plant species and soil properties will support the development of New Zealand specific values for use in the TFMS. It will also establish the relative sensitivity of protection of food safety in relation to other endpoints. This research will also provide provisional economic data on phytoremediation potential of cultivating hemp on landfarm-impacted soil. This study has been conducted to support food safety management, human and animal health protection and to protect the long-term trade interests of New Zealand. In addition, this research will provide quantitative evidence to establish the real level of environmental risk posed by landfarming.

## **1.5. Report Outline**

### **Chapter 2: Literature Review**

The literature review summarises knowledge of heavy metal accumulation and management in New Zealand soil, which involves:

- Heavy metals in New Zealand and their sources
- Factors influencing heavy metal accumulation in New Zealand agricultural soil
- Heavy metals management practices, strategy and regulations
- Risk of heavy metals in agricultural soil

### **Chapter 3: Methodology**

Chapter 3 describes the various method employed for the glasshouse study, laboratory analysis, and statistical analysis.

## **Chapter 4: Results**

Chapter 4 presents the data gathered from the various methodologies applied in chapter three.

## **Chapter 5: Discussion**

In Chapter 5 the results are interpreted and discussed with respect to the objectives defined in Chapter 1, and the background information presented in Chapter two.

## **Chapter 6: Conclusion and Recommendation**

In this final Chapter, an outcome relevant to problem statement, aims and objectives of the study is presented, and recommendations for further studies made.

## **Chapter 2 : Literature Review**

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### **2.1. Introduction**

This chapter reviews past related literature on heavy metals of concern in New Zealand agricultural soils and their risk to relevant endpoints (food safety, trade, ecological receptor and human/animal welfare). A review of various standard guidelines for assessing the risk of heavy metals to food safety, ecological receptors and animal welfare is also made. In addition, past studies on various heavy metal sources in New Zealand soils, factors influencing their accumulation in plant and soil and the proposed management approach are discussed to support the objectives of this study.

### **2.2. Metals of concern in New Zealand agricultural soil**

Common heavy metals found in contaminated soil are lead (Pb), chromium (Cr), arsenic (As), zinc (Zn), cadmium (Cd), copper (Cu), mercury (Hg) and nickel (Ni) (Evanko & Dzombak, 1997) while less common heavy metal contaminants are aluminium (Al), cesium (Cs), cobalt (Co), manganese (Mn), molybdenum (Mo), strontium (Sr) and uranium (U) (Mcintyre, 2003). Some of these heavy metals (Co, Cu, Fe (iron), Mn, Mo, Zn) are essential for organisms and plants thrive in non-toxic concentrations, while some (Pb, Cd, Hg and As) are not (Chibuike and Obiora, 2014). Cadmium contamination has attracted most concern in the New Zealand environment due to its presence as an impurity in phosphatic fertilisers while copper; zinc, lead, nickel, chromium, fluorine and arsenic are also of concern to New Zealand due to their presence in agrichemicals and sewage sludge (McClaren, 2007; Loganathan et al., 2003).

#### **2.2.1. Cadmium**

Cadmium is a naturally occurring trace element in the Earth's crust with an average background concentration ranging from 0.2 – 0.5 mg/kg in soils, although much higher

values may be found in some soils and rocks (Sneath, 2015). The cadmium concentration in New Zealand soils is low with a slow increasing rate of accumulation similar to international trading partners (MAF, 2011). The increasing concentration of cadmium in agricultural soils has been traced back to phosphate fertilizer application to agricultural soils while geologic processes contribute a non-significant amount to fertilized soils (MAF, 2011; Loganathan et al., 2003; Stafford et al., 2014).

Cadmium accumulation in agricultural soil was first identified in the 1990s when approximately 20% of sheep and cattle offal (liver and kidney) were found to be above the Maximum Permissible Concentration (MPC) of 1 mg/kg Cd fresh weight prescribed by the then Ministry of Health (Loganathan et al., 2003). An increasing concentration of cadmium in agricultural soil is a current trend world-wide due to the traceable level of cadmium in phosphate rocks (PRs) from which most phosphate fertilizers are produced (Sneath, 2015). In addition, phosphate fertilizer application to agricultural soils poses more significant threat to New Zealand while soil parent material (geologic sources) poses minimal/no significant threat to New Zealand soil (fertilized) (Roberts et al., 1994). Internationally and in New Zealand, human activities involving the use of phosphate fertilizers manufactured from phosphate rock are the dominant source of cadmium accumulation in agricultural soils (Roberts & Longhurst, 2002; Loganathan et al., 2003; Stafford et al., 2014; TRC, 2005).

Rocks of igneous and metamorphic origin have been reported to have lower cadmium concentrations while those of sedimentary origin have a much higher cadmium concentration (International Cadmium Association, 2015). Over the past four decades, cadmium has been the centre of focus in New Zealand as a food contaminant (Roberts et al., 1994). Cadmium retention in agricultural soils is influenced by factors such as

phosphate fertilizer use, the rate of application, soil factors and management practices (Grant, 2015; Mann et al., 2002) and these are discussed further in section 2.5.

### **2.2.2. Other metals of concern**

*Nickel:* Nickel is part of the transition elements in group VIII B of the periodic table with chemical characteristic similar to iron and cobalt (Christie & Brathwaite, 2014). It is rated 22<sup>nd</sup> in natural abundance among elements of crustal rocks and fifth in the earth (Christie & Brathwaite, 2014). The nickel concentration is generally found to be greater in ultramafic igneous rocks (0.1 – 0.3% Ni) than in silicic igneous rock (<0.006% Ni) (Christie & Brathwaite, 2014). In New Zealand, significant levels of nickel occurs significantly as nickel-copper sulphide mineral in the Riwaka Igneous Complex Mafic-ultramafic rocks in Graham Valley, Northwest Nelson (Christie & Brathwaite, 2014). It also occurs as nickel-sulphide mineralization of mafic-ultramafic rocks in the Cobb Valley (upper Takaka) and at Blue Mountain in Marlborough with insignificant occurrences found in mafic-ultramafic rocks of Westland, Otago, Fiordland and Southland (Christie & Brathwaite, 2014). Nickel can adsorb on to sediment or soil particles but is mobile under acidic conditions (Lenntech, 2016).

*Arsenic:* Arsenic is a metalloid element naturally occurring in mineral-bound forms in the earth's crust and can become more easily available through volcanic activity and rock weathering and through human activities like coal burning, smelting and arsenic-based wood additives etc. (CODEX, 2010). It is mostly found at concentrations of up to 50 mg/kg wet weight basis in most sea foods (seaweed, fish, shellfish and crustaceans) (CODEX, 2010).

*Copper:* Copper is a naturally occurring metal in soil that can also be introduced by human activities (Zovko & Romic, 2011). Mining activities, metal production, wood

production, phosphate fertiliser production and use of agrichemicals (Bordeaux mixture) in horticultural soils are human-influenced sources of copper in agricultural soils (Zovko & Romic, 2011; Lenntech, 2016). Most copper compounds complexes strongly with organic matter (Zovko & Romic, 2011). Water-soluble species pose a threat to the environment (Lenntech, 2016).

*Lead:* Lead is usually scarce but occurs naturally in the environment or through industry and transportation combustion processes (Zovko & Romic, 2011; Lenntech, 2016). Humans can be exposed to lead through food (such as vegetables, meats, grains, seafood, soft drinks and wine), water and air (especially cigarette smoke) (Lenntech, 2016). It is one of the highly toxic metals with damaging effects on human health (Lenntech, 2016).

*Cobalt:* Cobalt is a biological and chemically active chemical with potential of forming numerous compounds (Lenntech, 2016). It does not occur as a free metal but as a component of minerals (Lenntech, 2016). It's presence in the Earth's crust and in natural waters is of relatively low abundance (Zovko & Romic, 2011; Lenntech, 2016). The background level of cobalt in soil is 8 mg/kg but can be as low as 0.1 mg/kg and as high as 70 mg/kg (Lenntech, 2016). It supports the growth of blue-green algae (cyanobacteria) and other nitrogen fixing organisms (Lenntech, 2016). It is also essential to animals (in low concentration) as it is important in Vitamin B<sub>12</sub> (Zovko & Romic, 2011).

A study in China identified cadmium, nickel, copper, arsenic, mercury and lead as the most significant heavy metals affecting agricultural soil (MEP<sup>2</sup> & MLR<sup>3</sup>, 2014). The

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<sup>2</sup> Ministry of Environment Protection

<sup>3</sup> Ministry of Land Resources of the People's Republic of China

metals Cu, Pb, Zn, Ni, Cd, Hg and As are often found to be above maximum permissible limits of potentially toxic elements (0.3 mg/kg) (Lu et al., 2015).

A New Zealand study on heavy metal accumulation in farmed and non-farmed land identified the highest Cu enrichment in the top 2.5cm of farmed soil and insignificant concentration below soil top layer (Edmeades, 2013). In addition, a significant accumulation of Zn and As was found in pastoral soil (yellow brown loam) while other metals were within typical concentration ranges for global metal concentrations in agricultural soil (Edmeades, 2013). The ranges of heavy metals found in New Zealand pastoral and non-farmed soils reported by Edmeades (2013) is shown in Table 1. As, Cu, Pb and Zn concentrations in New Zealand have generally been concluded to be of pedogenic origin due to the small differences between farmed and non-farmed land (Edmeades, 2013).

**Table 1:** Ranges of Heavy metals in New Zealand farmed (pastoral) and non-farmed soils at 0 – 100mm (Edmeades, 2013).

Element	NZ farmed soils	Non-farmed soils
	<b>mg/kg</b>	
<b>As</b>	3-9	3 - 5
<b>Cd</b>	0.1-0.8	0.1 – 0.14
<b>Cr</b>	8-18	12 – 18
<b>Cu</b>	10-20	10 – 16
<b>Pb</b>	6-16	9 – 16
<b>Ni</b>	4-14	4 – 14
<b>Zn</b>	7-79	28 – 66
<b>Hg</b>	0.07-0.20	0.11 – 0.19

Another New Zealand study compared heavy metal accumulation in soil subject to different land uses in three regions (Appendix 3) of New Zealand namely Auckland, Waikato and Tasman (Gaw et al., 2006). The study reported higher concentrations of arsenic in orchard soils than other land use; higher cadmium and copper concentration in horticultural soil than other land uses while lead concentrations were generally higher in horticultural soils followed by orchard, vineyards, market gardens, with pastoral soils having the lowest concentration (Gaw et al., 2006). Identification of Cd, Pb; Cu and As (all components of past and present use of pesticides) in horticultural soils led to the recent recognition that horticultural soils in New Zealand are potentially contaminated sites and as such are now part of the HAIL<sup>4</sup> reported by the Ministry for the Environment (MfE<sup>5</sup>, 2004).

### **2.3. Risk of heavy metals accumulation in agricultural soil**

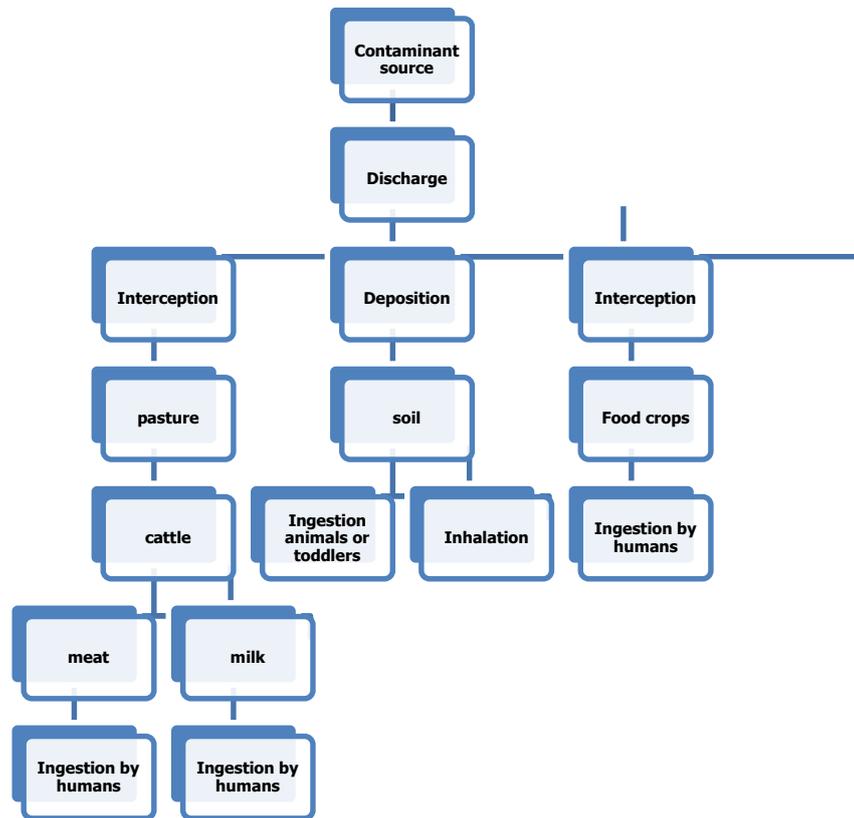
Excessive accumulation of heavy metals in agricultural soil can lead to elevated heavy metal uptake by food crops and hence a risk to human health via food crop consumption (Zhuang et al., 2009). The risk of heavy metals is associated with the extent to which they are in direct contact with relevant endpoints (human health, food safety, ecological receptors) (Jarup, 2003). Risk to food safety and human health is promoted by human influenced activities (discussed further in next section) involving fertiliser use, land application of wastes and pesticides use for agricultural activities (Lu et al., 2015). The risk of heavy metal accumulation in agricultural soil is promoted by mobilisation of the metals under specific soil physical and chemical conditions (Zovko & Romic, 2011). Assessing the risk of metals is crucial for the protection of different environmental media (Zovko & Romic, 2011). Metal speciation, bioavailability, bioaccumulation and toxicity are the key features to be considered in evaluating possible risk of metals on

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<sup>4</sup> Hazardous Activities and Industries List

<sup>5</sup> Ministry for the Environment

human health and the environment in general (Zovko & Romic, 2011). The level of heavy metal risk from agricultural soil to animals, humans and food safety is determined by the presence of an exposure pathway as shown in Figure 1 (Dinis & Fiuza, 2010).



**Figure 1:** Major exposure pathways of heavy metals in agricultural soil (Dinis & Fiuza, 2010)

### 2.3.1. Risk of heavy metals on food safety standards, trade and human health

The impact of heavy metals on food safety and human health is assessed by comparing heavy metals in food crops and soil with risk-based standards for the protection of different endpoints (Lu et al., 2015). Food standards cover an array of areas involving minimum and maximum contents of specific substances, labelling, storage, advertising, monitoring packaging, transport and record keeping with the aim of sustaining food

safety, fair trade and consumer health (Parliamentary Library, 2000). Food production is also part of food standards which addresses acceptable concentrations of microbiological, chemical and physical contaminants (Parliamentary Library, 2000). Because heavy metal at toxic level in food exposes consumers and animals to harmful effects (Lu et al., 2015), toxic metals routinely analysed in the New Zealand Total Diet Survey (TDS) are arsenic, cadmium, lead, mercury and tin while the essential nutrients also analysed are iodine, selenium and Zinc (Parliamentary Library, 2000). A Taranaki Regional Council study reported pasture as a major exposure pathway of micro (heavy metal) and macro element contamination in food and animals (Edmeades, 2013). The impacts of heavy metals on human health is summarised in Table 2.

**Table 2:** Impact of heavy metals on human health

Metals	Effects on human health
<i>Cadmium</i>	Cadmium can be toxic at high levels or at continued exposure and inhalation (MAF, 2011) and can pose threat to humans through consumption of contaminated food crops or offal (kidney and livers) of exposed animals (MAF, 2011). Long term exposure to cadmium causes renal tubular damage, with likely effects on bone and fractures (Jarup, 2003). Cadmium effects can also be experienced at lower exposure level than expected (Jarup, 2003).
<i>Nickel</i>	Nickel is an essential element at small concentration in animal food stuff but carcinogenic at the exceedance of maximum tolerable levels (Lenntech, 2016). In addition, humans are exposed to nickel by breathing contaminated air, drinking water, food, smoking and skin contact with nickel-contaminated soil or water (Lenntech, 2016).
<i>Copper</i>	Copper is essential to humans at acceptable levels and can be found in many food substances, drinking water and air (Lenntech, 2016). In addition, continued exposure to copper can result in; headache,

	diarrhoea, liver, kidney damage and irritation of nose, mouth and eyes (Lenntech, 2016). Limited or excessive copper can affect crop production (Wuana & Okieimen, 2011).
<b><i>Lead</i></b>	Lead is not essential to human function; rather its presence can cause interruption of the biosynthesis of haemoglobin, blood pressure rise, kidney damage, miscarriage/subtle abortion, brain damage, deterioration of fertility in men, minimata disease in Japan, nervous system breakdown and behavioural interruptions in children (Lenntech, 2016; Wuana & Okieimen, 2011).
<b><i>Cobalt</i></b>	Cobalt is essential to human growth as part of vitamin B12, in treatment of anaemia for pregnant women because it promotes production of red blood cells (Lenntech, 2016). However, extreme levels of cobalt in human body can cause health deterioration, lung effects, and pneumonia (Lenntech, 2016). Fruits and seeds can also accumulate cobalt in contaminated soils (Lenntech, 2016).
<b><i>Chromium</i></b>	Chromium relates to allergic dermatitis in humans and its also carcinogenic (Wuana & Okieimen, 2011).
<b><i>Zinc</i></b>	Excessive accumulation of zinc in soil can alter the activities of microorganisms and earthworms which will eventually affect organic matter breakdown (Wuana & Okieimen, 2011).
<b><i>Mercury</i></b>	Mercury causes kidney damage (Wuana & Okieimen, 2011).
<b><i>Arsenic</i></b>	The most lethal form of arsenic is the inorganic arsenic (III) and (V) compounds and arsenic trioxide known as rat poison (CODEX, 2010). Humans have often been exposed to inorganic arsenic in drinking water and it's been known to inflict a lifetime induced skin cancer (CODEX, 2010).

Major food products from New Zealand agricultural soils are exported, providing half of its export earnings (Parliamentary Library, 2000). CODEX (2010) and FSANZ<sup>6</sup> standards are applied to ensure security of food for international trade in New Zealand (MPI, 2012).

#### **2.3.1.1. Maximum levels of contaminants in food and feed (CODEX Alimentarius)**

CODEX Alimentarius is an international code of independent standards for managing food additives, pesticides, slag, veterinary drugs and other issues of threat to consumer food safety (CODEX, 2010). It also includes rules and guidelines to enhance fair practices in food trade and as well suggests an international code of hygiene and technological practices (CODEX, 2010). CODEX Alimentarius defines contaminants as any unintentional substance identified in food that is not present as a result of production (including agricultural production), manufacture, processing, preparation, treatment, packaging, transport or handling (CODEX, 2010). The term however, excludes insect fragments, rodent hairs and other extraneous matter (CODEX, 2010).

Assessing the potential risk of food contamination using CODEX maximum levels requires consideration of specific criteria involving toxicological information, analytical data, intake data and technological considerations (see Appendix 4 for more details) (CODEX, 2010). CODEX guideline and maximum level of the heavy metal contaminants in food products examined in this study is summarised in Table 3.

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<sup>6</sup> Food Standards Australia New Zealand

**Table 3:** CODEX guideline for consumer food protection (CODEX, 2010)

<b>Total heavy metals</b>	<b>Consumer food (mg/kg)</b>
<b>Cadmium</b>	0.2
<b>Lead</b>	0.3
<b>Arsenic</b>	0.1
<b>Mercury</b>	0.1

### **2.3.1.2. Food Standards Australia New Zealand (FSANZ)**

The maximum level of contaminants in food set by food standards Australia New Zealand provides effective risk management functions to manage exceptional foods that significantly contribute to total dietary exposure of contaminants (FSANZ<sup>7</sup>, 2013). FSANZ maximum levels ensure that protection of public health and safety is reasonably achievable through safe production and resource management practices (FSANZ, 2013). The maximum levels also cover Australia and New Zealand's international trade commitment under the World Trade Organisation's Agreement on the Application of Sanitary and Phytosanitary Measures and the Agreement on Technical Barriers to Trade (FSANZ, 2013). Maximum levels of metal contaminants in leafy vegetables for the protection of public health and safety by FSANZ is summarised in Table 4.

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<sup>7</sup> Food Standards Australia New Zealand

**Table 4:** Tolerable limits of contaminants in consumer food for the protection of public health, safety and trade (FSANZ, 2003)

<b>Heavy metals</b>	<b>Consumer food (mg/kg)</b>
<b>Cadmium</b>	0.005
<b>Lead</b>	0.01
<b>Arsenic</b>	0.01
<b>Mercury</b>	0.002
<b>Copper</b>	0.01
<b>Zinc</b>	0.01

### **2.3.2. Risk of heavy metals on ecological receptors**

The importance of different ecological receptors is somewhat dependent on land use type (Cavanagh, 2014). Protection of ecological receptors is similar to the protection of land productivity (MPI, 2012). Key ecological receptors of high relevance are microorganisms, plants and soil invertebrates (Cavanagh, 2014; MPI, 2012). Higher animals (livestock) may also be affected when they consume prey species that are predisposed to contaminant accumulation (MPI, 2012). Regional Councils are currently working on developing specific national soil guideline values for the protection of ecological receptors from metal contamination in New Zealand (Cavanagh, 2014). Contaminants of high risk that are considered for the development of soil guideline values are both inorganic (As, Cu, Cd, F, Pb and Zn) and organic (DDT, total petroleum hydrocarbon and polycyclic aromatic hydrocarbon) (Cavanagh, 2014). Current soil guideline values used for the protection of ecological receptors from Cd in New Zealand are shown in table 5.

**Table 5:** Soil guideline values developed for the protection of ecological receptors from bioavailable cadmium contamination in New Zealand (NZWWA, 2003; Cavanagh, 2006b)

Value name	Cadmium (mg/kg)	Source
Soil limit	1	NZWWA, 2003
Minimal risk	1	Cavanagh, 2006b
Serious risk	12	“
Minimal risk (microbial)	6	“
Serious risk	86	“

#### 2.3.2.1. Microorganism activity in land impacted by drilling waste

Soil microbiological activity, measured by enzymatic activities, is vital to nutrient cycling and both the mineralisation and transformation of organic matter and plant nutrients in the soil environment (Dick & Tabatabai, 1993). Soil microbial activities are susceptible to natural and anthropogenic disruptions (Dick, 1997). Dehydrogenase activity of a soil is used to quantify soil microbial activity as an indication of the total oxidative activity of microorganisms (Gregory et al., 2015). Soil enzymatic (dehydrogenase) activity measurement can be used to estimate the extent to which the normal function of soil is degraded by contaminants (Gregory et al., 2015).

The broad metabolic diversity and hydrocarbon degrading potential of soil microbial populations are reduced in contaminated soils (Silva-Castro et al., 2015). The ability of soil microorganisms and their biological activity to utilise carbon and energy from hydrocarbons in landfarm-impacted soils is the basis for bioremediation (Bento et al., 2005). Soil microorganisms (heterotrophs) require a carbon source for cell growth and energy supply to sustain metabolic activities supporting their growth (Silva-Castro et

al., 2015). They also require nitrogen and phosphorus for cell growth (Silva-Castro et al., 2015). Based on their carbon and energy requirements, hydrocarbons in soil will provide a source of carbon and energy, but, at same time, cause accelerated exhaustion of available supplies of essential inorganic nutrients such as nitrogen and phosphorus (Silva-Castro et al., 2015). Silva-Castro et al. (2015) confirmed increased microbial activity at a landfarmed (hydrocarbon) site with initially high biological activity. The authors confirmed the necessity of assessing soil characteristics prior to landfarming so as to enhance efficient biodegradation of oil and gas waste. In addition, they also reported improvement in microbial activities with the addition of nutrients (NPK fertiliser). However, any heavy metal toxicity in soil reduces the microorganism population which affects organic matter decomposition and a decline in the concentration of available soil nutrients (Chibuike & Obiora, 2014).

Cavanagh et al. (2014) identified drilling mud as being highly toxic to earthworms which stresses the indigenous soil microbial population in impacted soils. However, they attributed this to an application of mud waste in excess of the acceptable limits. Earthworm toxicity from drilling mud is due to high salt concentrations (Cavanagh et al., 2014). Initial micro- and macro-organism disturbance may occur at an early stage of hydrocarbon introduction to soil but decreases with time due to adaptation (Cavanagh et al., 2014).

Dehydrogenase activity is a measure of an enzyme released during the respiration pathways of both aerobic and anaerobic microorganisms and is used to measure biological activity in soil (Jeyakumar et al., 2008). A study of microbial activity on cultivated and natural soil (Table 6) suggests significant soil microbial activity improvement over natural background levels from application of organic waste and crop

residue (Pajares et al., 2011). This is similar to a Marin et al. (2005) study that reported soil improvement with drilling waste application. Gregory et al. (2015) reported a stable dehydrogenase activity (Table 6) in an old sheep dip site (highly contaminated with Arsenic) at an initial stage of a six months glasshouse trial and an increase in dehydrogenase activity with the addition of 350<sup>0</sup>C biochar relative to the control (sheep dip site) soil. He also observed a decrease in dehydrogenase activity with time.

**Table 6:** Comparing natural background level of dehydrogenase activity in different land use types (Pajares et al., 2011)

Land use type	DHA (ug/g)
Conventional	0.58 <sub>b</sub> (0.14)
Improved conventional	1.25 <sub>a</sub> (0.08)
Organic farming	1.35 <sub>a</sub> (0.16)
Fallow	0.59 <sub>a</sub> (0.01)
Natural soil	0.67 <sub>b</sub> (0.08)
Contaminated soil/sheep dip site (Gregory et al., 2015)	100

*Values in bracket represents the standard deviation; Conventional land use:* land ploughed every year with fertiliser application with exportation of crop residue; *Organic farming:* use of cow, poultry and compost and crop rotation; *Improved conventional:* mulching with crop residue ad moderate application of inorganic fertiliser on crop demand and crop rotation; *Fallow:* one year fallow with low fertiliser and cattle grazing; *Natural soil:* soil under native grass cover.

Jeyakumar et al. (2008) reported 50% reduction (ED<sub>50</sub>) in soil dehydrogenase activity with a solid phase exchangeable Cu (410 mg/kg) and Zn (670 mg/kg) concentration, which is above the soil guideline for safe application of drilling waste. Akmal & Jianming (2008) reported a lead concentration of 1000 mg/kg as the ecological dose

50% (ED<sub>50</sub>). Ecological dose represents the concentration of toxic metal that will initiate 50% reduction in soil microbial activity (Akmal & Jianming, 2008).

Marin et al. (2005) reported higher dehydrogenase activity in landfarm-impacted soil (Table 7) than a control (uncontaminated) soil in semi-arid Mediterranean areas, although a decrease in microbial activity in landfarmed soil was recorded in the first five months, it stabilises thereafter at about twice the control activity. However, over the trial period (11 months), the DHA does not get down to the control levels. It is likely that dehydrogenase activity decreases with time in landfarmed soil due to contaminant degradation by soil microorganism and therefore reduction in their hydrocarbon food source (Marin et al., 2005).

**Table 7:** Dehydrogenase activity (DHA) in landfarming and control pots over time (Marin et al., 2005)

Time (months) after Oil-sludge application	DHA (ug/g)	
	Control	Landfarming
1	0.073	0.197
3	0.032	0.156
5	0.071	0.099
7	0.035	0.091
9	0.043	0.089
11	0.039	0.063
<b>MDS<sup>8</sup> P&lt;0.05</b>	±0.010	±0.022

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<sup>8</sup> Multidimensional scaling

## **2.4. Heavy metal sources of concern in New Zealand**

### **2.4.1. Heavy metal associated with phosphate fertiliser use**

Phosphate fertilizer contains cadmium and fertiliser application has resulted in cadmium accumulation in soils, with resultant uptake by plants (Mann et al., 2002). Its accumulation in soil depends on the initial cadmium concentration of phosphate rocks utilised for phosphate fertiliser production (Grant, 2015). The main cadmium vectors to New Zealand pasture land is direct application of reactive phosphate rocks or the acidulated form involving single superphosphate (SSP), partially acidulated phosphate rock (PAPR), triple superphosphate (TSP), or diammonium phosphate (DAP) (Loganathan et al., 2003). Appendix 1 presents more details on the phosphorus, cadmium and fluorine concentrations in various reactive phosphate rock sources.

Low cadmium-containing phosphate rocks are scarce with uncertain availability (MAF, 2011). New Zealand previously sourced phosphates fertilizers from Nauru and Christmas Island, phosphate rocks known to contain a high natural concentration of cadmium, but recently, the cadmium content of New Zealand fertilizers has been minimised through blending with lower cadmium content rocks (TRC, 2005). The lower cadmium-containing phosphate rock is sourced from open-pit mines in Khouribga, near Casablanca in Morocco where marine life remains of ancient times are deposited (Roberts, 2015). This phosphate rock is washed and dried prior to shipment to New Zealand (Roberts, 2015). Rothbaum et al. (1986) reported lower cadmium accumulation in agricultural soil with a long history of low cadmium containing phosphate fertilizer (DAP) application than with a higher cadmium containing fertilizer (SSP) in Europe. SSP produced from sedimentary rocks like Nauru and Christmas Island parent rocks contain a higher cadmium concentration (Williams & David 1973; Loganathan et al., 1995) than those of igneous origin due to coprecipitation of cadmium (in place of

calcium in phosphate compounds) formed during sedimentary deposition and volatility of cadmium at temperature above 765<sup>0</sup>C at which igneous rock are formed (Traina, 1999; Loganathan et al., 2003). The high Cd of Nauru and Christmas Island rocks is a result of their being the product of accumulation of bird guano over millennia (Loganathan et al., 2003). Birds are near the top of the marine food chain and this food chain concentrates Cd (Cd in marine sediments co-varies with P and is an ocean productivity proxy indicator) (Loganathan et al., 2003) Maximum permissible concentration of cadmium in phosphate fertilizer has been progressively reduced to 280 mg Cd/kg (Table 8) from what it was (420 mg Cd/kg) prior to 1995 (Stafford et al., 2014).

**Table 8:** Implemented MPC of Cadmium in P fertilizer in New Zealand (adapted from Loganathan et al., 2003)

<i>Country</i>	<i>Cd limit (mg/kg P<sup>a</sup>)</i>	<i>Effective year</i>
<b>New Zealand</b>	420	July 1995 – Dec. 1996
	340	Jan. 1997 – Dec. 1999
	280	Jan. 2000 till date

a = (mg Cd/kg P) x (% P in fertiliser) / 100 = mg Cd/kg fertilizer.

#### **2.4.2. Heavy metals associated with landfarming activities**

Landfarming is a waste-disposal activity practiced in the Taranaki region New Zealand that aims to naturally bioremediate hydrocarbon-containing waste from oil exploration and production well drilling by surface, sub-surface and mix-bury-cover application to land (Cavanagh, 2015). Oil and gas drilling muds are incorporated into re-shaped sand dunes which are then used for pasture growth (Edmeades, 2013; Cavanagh, 2015).

Landfarming in Taranaki is controlled by resource consent administered by the Taranaki Regional Council (Edmeades, 2013). The Ministry for Primary industry (MPI) New Zealand recently released a report titled “*land application of waste from oil and gas wells*” which concludes that landfarming poses no risk to food safety or animal welfare when grazing and crop harvesting is carried out within safe soil quality standards and when waste is applied to subsoil underlying a top soil (Cavanagh, 2015). MPI standards set for the efficient application of oil and gas waste to land is such that food safety and animal welfare is maintained (Cavanagh, 2015). The drilling mud contains contaminants such as petrochemical residues, barium, heavy metals and salts (Edmeades, 2013). Specifically, drilling mud slurry contains rock cuttings, bentonite, and counteragent additives (barium sulphate) used for lubricating the bit or for the control of the in-well pressure conditions (Edmeades, 2013; Cavanagh, 2015).

#### **2.4.2.1. Heavy metal concentration of drilling waste**

Drilling waste comprises drilling fluid (either water based, non-aqueous, oil based or synthetic based) and drill cuttings (Melton et al., 2000). Components of Water based fluid (WBF) are salt, water, barite, bentonite and other additives and the concentration of all these components depends on the volume of the fluid (Melton et al., 2000). A 1190 kg/m<sup>3</sup> WBF contains 76% wt water, 15% barite, 7% bentonite, 2% salt and other additives with barium dominating the heavy metal content of WBF waste (NRC , 1983). Other trace metals are found in very low concentrations (Melton et al., 2000). Metals of most concern in relation to potential toxicity in drilling fluids are arsenic, barium, chromium, cadmium, iron, lead, mercury, nickel and zinc (Neff et al., 1987; 2000). A proportion of the metal load is introduced intentionally to drilling mud as metal salts or organo-metallic compounds while some occurs as impurities in major mud ingredients, mostly barite and clay (Neff, 2005). Table 9 shows the elemental components of drilling

mud waste from a typical Nigerian oil company with a greater proportion of macro elements than micro elements present.

**Table 9:** Elemental composition of water based fluid (WBF) and oil based fluid (OBF) of a drilling mud waste from two oil exploration sites (Dibi and Ewan) in Nigeria (Adewole et al., 2010).

Elements	OBF (mg/kg)		WBF (mg/kg)	
	Dibi	Ewan	Dibi	Ewan
<b>Iron</b>	349.50	349.50	349.50	349.50
<b>Calcium</b>	193.72	193.72	193.72	193.72
<b>Magnesium</b>	87.50	87.50	87.50	87.50
<b>Potassium</b>	49.31	49.31	49.31	49.31
<b>Lead</b>	2.38	2.38	2.38	2.38
<b>Nickel</b>	Present	Absent	Present	Absent
<b>Copper</b>	Present	Present	Present	Present
<b>Zinc</b>	4.67	<1.0	<1.0	<1.0
<b>Chromium</b>	<1.0	<1.0	1.20	<1.0

Table 10 presents a summary of reported heavy metal concentrations in water-based drilling mud for selected international oil exploration operations. This general background information on heavy metal concentration from international sites (Nigeria, Norway, US Gulf of Mexico and Southern California) cannot be directly compared to a New Zealand context due to a lack of similar data for this country. However, zinc, chromium and lead showed the least concentrations in Nigerian drilling mud. In New Zealand, Cu and Zn have been reported to occur at elevated concentrations in landfarm-impacted soil (Cavanagh, 2015). There is also potential for the addition of these elements to benefit the soil. These elements may be essential micronutrients and where drilling waste is applied to soils where Cu and Zn are deficient (Cavanagh, 2015).

**Table 10:** Some heavy metal concentration of WBF (drilling mud) (Neff, 2005 & 2008).

Metals	Heavy metal concentration (mg/kg Dry weight)		
	Southern <sup>9</sup> California	US Gulf of Mexico <sup>10</sup>	Norway <sup>1</sup>
Barium	53,900	524,000	NA
Silver	0.37	-	-
Arsenic	10	-	-
Cadmium	1.17	0.77	0.05
Chromium	91	6.5	40
Copper	24	88	86
Mercury	0.09	5.9	0.05
Nickel	39	-	-
Lead	23	243	18
Vanadium	76	-	-
Zinc	167	167	1211

#### 2.4.2.2. Chemical properties of drilling waste

Drilling waste often has an elevated pH due to the lime, caustic soda, soda ash and sodium bicarbonate components added (C.Cure Solutions Ltd, 2012). In addition, drilling waste also has elevated chemical oxygen demand, very low redox potential, a high exchangeable sodium concentration and high electrical conductivity. These parameters suppress natural biodegradation of hydrocarbons in the drilling waste (C.Cure Solutions Ltd, 2012).

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<sup>9</sup> Neff (2005)

<sup>10</sup> Neff (2008)

#### **2.4.2.3. Plant response to heavy metals in landfarm-impacted soil**

A high percentage of heavy metals found in drilling mud originates from trace impurities in barite (an insoluble sulphate salt), bentonite clay or drill cuttings sourced from the levels reached in the drill holes (Neff, 2008). However, the heavy metals of concern (cadmium, lead, zinc, chromium, copper and mercury) contained in barite ( $\text{BaSO}_4$ ) have restricted environmental mobility, resulting in minimal toxicity to plants and animals (Neff, 2002ab). Mobility of these metals from the barite solid phase to a biologically accessible form (dissolved ions or ion complexes) depends on dissolution of the solid phase and is influenced by the accessibility of metals to the solid-water interface (Neff, 2008). Solubility of heavy metals in barite solid phase through weathering processes or where influenced by root exudates, facilitates its accumulation by plants (Blaylock & Huang, 2000). Heavy metal at toxic levels in soils can lead to replacement of essential nutrients at soil surface cation exchange sites and increased bioavailability of these metals leads to cell structure damage (Chibuiké & Obiora, 2014). For example, zinc accumulation in soil planted with ryegrass (*Lolium perenne* L.) can lead to zinc accumulation in plant leaves, growth inhibition, reduced plant nutrient content and reduced potentials for photosynthetic energy conversion (Bonnet et al., 2000).

A New Zealand study of the extent to which landfarming is “fit for dairy and pasture growth” supported the use of drilling mud for pasture improvement and dairy farming (Edmeades, 2013). This study revealed that heavy metal accumulation in clover and ryegrass grown on three different landfarm-impacted sites in the Taranaki region (Table 11) were within typical concentrations for New Zealand pasture with a few exceptions. Zn was higher than normal but posed no significant threat to plants; Co was above the minimum level required for optimum pasture growth; and Cr was above normal soil

values for Geary site only (both irrigated and non-irrigated). The conclusion of this study was that landfarming areas are fit for pasture (clover and ryegrass) growth under irrigated and fertile soil conditions in New Zealand and are capable of producing at least 15 tonnes DM/ha annually (Edmeades, 2013).

**Table 11:** Heavy metal concentrations in mixed-pasture from three sites in Taranaki collected on 5th August 2013 (Edmeades, 2013)

Site	Heavy metal concentration (mg/kg)								
	As	Zn	Cu	Cd	Co	Hg	Ni	Ba	Cr
<b>Schrider</b>	<0.1	31	6.4	0.022	0.16	0.013	<1	42	0.460
<b>Geary (irrigated)</b>	<0.1	32	7.6	0.011	0.87	<0.01	<1	74	0.750
<b>Geary non-irrigated</b>	<0.1	28	9.2	0.025	0.46	0.011	<1	>100	0.600
<b>Brown</b>	<0.1	31	9.3	0.073	0.18	0.011	<1	71	0.520
<b>Typical<sup>11</sup></b>	0.07 – 0.24	10 - 20	5 - 10	0.03 – 0.29	0.04 – 0.10	Ng	0.10 – 0.20	ng	0.31 – 0.49

ng = not given

Plant uptake of heavy metals does not show specific patterns in contaminated soil relative to clean soils and this is evident in a study (Table 12) that compared the concentration of heavy metals in pasture (ryegrass) between clean (uncontaminated soil) and oil waste contaminated soil (Kostecki, 1999). Although the results of the study does not show a specific pattern of accumulation, ryegrass showed an elevated concentration of zinc and manganese but concentrations were still within the normal or permissible limit for plants (Kostecki, 1999).

<sup>11</sup> Typical concentration in pasture grown on New Zealand soil

**Table 12:** Metal accumulation in ryegrass cultivated in clean and land with drilling mud waste applied after 12 months of landfarming (Kostecki, 1999)

Element	Clean soil (mg/kg)	land with drilling mud waste applied (mg/kg)
Pb	4.98	4.31
Cu	12.3	12.9
Zn	30.1	38.4
Cr	15.6	10.1
Ni	10.0	9.3
Mn	80.6	91.9
Co	<0.1	<0.1
Mo	4.7	2.5

#### 2.4.2.4. Heavy metals accumulation in landfarm-impacted soil

Metals exist either as hydrated ion or in association with other soil components such as exchangeable ions sorbed on the surface of inorganic solids, nonexchangeable ions and insoluble inorganic metal compounds e.g. carbonates and phosphates, soluble metal compounds or free metal ions in the soil solution, metal complexes of organic materials, and metals bound to silicate minerals (Marques et al., 2009). Edmeades (2013) compared the heavy metal concentration of average farmed and non- farmed soils each with that of three landfarmed sites and concluded that heavy metals such as Cd, Cr, Cu and Ni accumulate more in the top soil (0 – 100 mm) relative to the rest of the disturbed soil profile (100 – 200 mm). The report also concludes that soil heavy metal concentrations in the three studied landfarm-impacted sites (Table 13) were at the lower end of the ranges for both farmed (dairying) and non-farmed lands.

**Table 13:** Comparison of heavy metal concentration (mg/kg) in a New Zealand pastoral soil and non-farmed soils (0 - 100mm) and the soils (0-75mm) of three landfarmed Taranaki sites (Edmeades, 2013)

Element	Ranges for NZ farmed and (non-farmed soils) mg/kg	Sites (mg/kg)			
		Schrider	Geary		Brown
			Non Irrigated	Irrigated	
As	3-9 (3-5)	<2	<2	<2	2
Cd	0.1-0.8 (0.1 – 0.14)	0.11	<0.1	<0.1	<0.1
Cr	8-18 (12-18)	11	11	11	8
Cu	10-20 (10-16)	11	20	13	21
Pb	6-16 (9-16)	1.8	3	1.4	3.6
Ni	4-14 (4-14)	5	5	5	4
Zn	7-79 (28-66)	55	53	57	57
Hg	0.07-0.20 (0.11-0.19)	<0.1	<0.1	<0.1	<0.1

#### 2.4.3. Heavy metals associated with the use of agrichemicals on horticultural soil

The use of agrichemicals and pesticides in New Zealand orchard and horticultural soil has been reported as the main source of trace elements like Cu, As and Pb across three regions (Auckland, Waikato and Tasman) in New Zealand (Gaw et al., 2006). Arrays of agrichemicals with potential contaminants as active ingredients have been applied extensively on horticultural soils in New Zealand for more than 100 years (Gaw et al., 2006). Lead arsenate, calcium arsenate and copper arsenate were part of the first spectrum of pesticides used both in New Zealand and internationally for the control of chewing insects on fruits, vegetables and ornamentals (Cunningham & Cotter, 1933). These pesticides are now banned in New Zealand while fungicides containing copper were historically and currently used in New Zealand (Gaw et al., 2006). Some mercury

compounds have also been widely used due to mercury's antifungal and antibacterial features (Gaw et al., 2006). Zinc is a component of some fungicides like Propineb<sup>®</sup> and Maconzeb<sup>®</sup> also widely used for bloat control, as soluble Zn in water trough and in Zn paste used as a drench (Gaw et al., 2006).

#### **2.4.4. Heavy metals associated with land application of biosolids**

Land application of livestock dung, effluent, compost and municipal waste can result in the accumulation of heavy metals such as As, Cd, Cr, Cu, Pb, Hg, Ni, Se, Mo, Zn in soil (Basta et al., 2005). These contaminants originate from animal feed or industrial processes and repeated application of highly concentrated biosolids to land can result in excessive accumulation of these metals in soil (Wuana & Okieimen, 2011). In New Zealand, land treated with biosolids has shown slightly elevated concentrations of Ni, Cd and Zn in drainage leachates (Keller et al., 2002; McLaren et al., 2004).

### **2.5. Factors influencing heavy metal accumulation in soil**

#### **2.5.1. Heavy metal characteristics**

The chemical behaviour of metal in soil is determined by its chemical form which is a function of environmental conditions (Zovko & Romić, 2011). Metal speciation is a vital characteristic that determines metal toxicity and potential for accumulation in the soil environment (Zovko & Romić, 2011). Chemical speciation of a metal is an explicit form defined by different isotopic composition, complexions and oxidative or electron state (Manouchehri et al., 2006). It is also a means of identifying and determining various chemical and physical forms of element present in a sample (Wang et al., 2006). Metals in cationic forms possess high binding ability to negatively charged soil colloids which makes them less bioavailable but more likely to accumulate in soil (Zovko & Romić, 2011). Metals in anionic complexes are generally present in soil solution, making them bioavailable and easily leached from soil (Zovko & Romić, 2011). Some

of the metals that exist as anionic complexes include cobalt, nickel, iron, copper, chromium, zinc, vanadium and aluminium (Clark, 2003).

Metal solubility is a characteristic that determines its availability in soil for plant uptake (Gray & McLaren, 2006). Bioavailability is a term used to describe the solution phase of metals or the freely available metal fraction that a plant can easily uptake (McGrath & Semple, 2010). Metal bioavailability is an intricate issue that depends on factors relating to the soil matrix, plant characteristics and environmental conditions (Zovko & Romic, 2011). Bioavailability of metals in soil influences the residual concentration in soil where low bioavailability suggests soil accumulation over time to a level that may pose significant threat to humans and animals (Kirkham, 2006).

#### **2.5.2. Soil characteristics**

Abstraction of metals from agricultural soil by plants depends on their concentration in soil, crop varieties and metal bioavailability which is a function of soil properties (Grant, 2015). Cadmium bioavailability in soil (Table 14) is influenced by soil chemical and biological properties including soil pH, organic matter content, ionic strength of the soil solution, zinc availability, rhizosphere chemistry and mycorrhizal relationships (Grant, 2015; Loganathan et al., 2003; Kirkham, 2006). The accumulation of other metals (like Ni, Cu, Cr, Pb and Zn) in soil is also influenced by the characteristics described in table 14 for Cd (Gray & McLaren, 2006).

**Table 14:** Soil factors influencing cadmium bioavailability and plant uptake (Gray & McLaren, 2006)

<b><i>Soil pH</i></b>	Low soil pH influences cadmium removal in soil through plant absorption while increase in pH reduces cadmium bioavailability in soil (Kirkham, 2006; Mann et al., 2002). The influence of increasing soil acidity on cadmium bioavailability is evident in the study of Mann & Ritchie (1993), where increasing soil acidity elevated cadmium solubility by 95% and bioavailability in Western Australia.
<b><i>Soil organic matter</i></b>	Another factor that determines cadmium bioavailability in soil is the availability of organic matter in surface and sub-surface layer which increases mobile cadmium ion adsorption and thereby reducing its bioavailability to plants (Kirkham, 2006, Mann et al., 2002). Bioavailability of cadmium can be reduced by the presence of soil solutes (chloride) which forms both organic and inorganic complexes with organic matter (Naidu et al., 1994).
<b><i>Zinc competition</i></b>	Due to similarity in the chemical structure of zinc and cadmium they tend to compete with each other with zinc possessing higher advantage of suppressing cadmium uptake by plants thereby encouraging cadmium accumulation in soil (Kirkham, 2006; Loganathan et al., 2003). The influence of zinc on cadmium accumulation was described by Homma & Hirata (1984) who observed a two-fold uptake of zinc over cadmium uptake by rice seedlings at equally high concentrations of both metals. This implies that zinc deficiency promotes Cd uptake by plants (Homma & Hirata, 1984).
<b><i>Soil mineralogical and chemical features</i></b>	Cadmium accumulates more in fertilized (phosphate fertilizer) clay soil (clay and sesquioxides) than sandy soils and this may be a result of the adsorption capacity of clay-minerals and low retention of cadmium in sandy soils which may predispose it to leaching or plant uptake (Mann et al., 2002). Soil chemical features and ionic strength depends largely on the type of parent material, weathering conditions, mineral components, soil amendments and management activities (Naidu et al., 1994).
<b><i>Rhizophere chemistry and mycorrhizal association</i></b>	In phosphorus deficient soils, release of root exudates and acidification (through proton extrusion) by plants encourages cadmium availability and uptake by plants (Grant, 2015). Phosphorus enrichment in soil also controls development of mycorrhizal associations which ensure cadmium availability for plant uptake by reducing pH (Grant, 2015).

### 2.5.3. Plant characteristics

Plant species and genotype influences the rate of heavy metal uptake from contaminated soil (Khan et al., 2000). Plants have developed extremely specific and highly efficient means of obtaining essential micronutrients from the soil environment even at low metal concentrations (Tangahu et al., 2011). Factors facilitating plant metal uptake efficiency involves plant induced pH changes and redox reactions, and the exudation of chemicals (chelating agents) into rhizosphere (Tangahu et al., 2011). These factors ensure a plant's ability to solubilise and take up micronutrients from very low metal concentrated soils or even from nearly insoluble precipitates (Tangahu et al., 2011). Specific plant-containing proteins embedded in the plant cell plasma membrane also facilitate their metal uptake and they involve (a) proton pumps (ATPases that use up energy and generate electrochemical gradients), (b) Co- and antitransporters (proteins that utilise the electrochemical gradients generated by ATPases to drive the active uptake of ions) and channels (proteins that promote the transport of ions into cells) (Tangahu et al., 2011). Plants accumulate metals first in their root system and then translocate these into shoots and plant biomass and little is known about this plant mechanism (U.S DoE<sup>12</sup>, 1994). Heavy metal uptake by plants is usually within the concentration range of 10 – 15 mg/kg, except for plants regarded as hyperaccumulators with the ability to accumulate toxic metals ions at levels within or above 1000 mg/kg (U.S. DoE, 1994). These hyperaccumulating plants usually accumulate and store metals in their vacuole (U.S. DoE, 1994). Hyperaccumulating plants (i.e >1000 ppm) are those that can achieve a shoot to root metal concentration ratio greater than one (Tangahu et al., 2011). Those plants are expected to survive in highly toxic environments with little maintenance and may have the ability to yield normal biomass (Salido et al., 2003).

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<sup>12</sup> United States Department of Energy

#### **2.5.4. Rate of phosphate fertiliser application**

Cadmium accumulation in agricultural soil is influenced by both the rate, and regularity of phosphate fertilizer application, and the rate of removal (crop uptake, leaching losses, etc) from soil (Grant, 2015). This observation is based on Australian (Williams & David, 1976) and New Zealand (Roberts et al., 1994; Loganathan et al., 1995; Loganathan et al., 2003) studies where application of phosphorus fertilizer containing cadmium between 20 and 50 mg/kg to pastoral land resulted in a significant increase in the cadmium concentration of surface soils. Cadmium accumulation in agricultural top-soil has been correlated with top-soil phosphorus concentration and this reflects a long history of phosphate fertilizer use (Loganathan et al., 2003). There is also a correlation between cadmium accumulation in soil, rate/type of phosphatic fertilizer use and the properties of soils receiving the fertilizers (Rothbaum et al., 1986; Mann et al., 2002; Gray et al., 1999). Increased application of phosphate fertilizers to cadmium enriched soils also results in more soil Cd accumulation and less phyto-availability (loss through crop) of cadmium due to formation of less soluble complex ionic structure with phosphorus (Grant, 2015).

#### **2.5.5. Tillage effects**

Accumulation of cadmium in soil may also be influenced by cultivation/tillage factors (Mann et al., 2002). Cadmium accumulates less in the surface layer of intensively cultivated farm land and more in the surface layer of uncultivated farmland (Mann et al., 2002). Mann et al. (2002) observed higher cadmium accumulation in the 0 – 2 cm layer and lower accumulation at increasing depth (2 – 5 cm and 5 – 10 cm) for fertilized (phosphate fertilizer) and uncultivated orchard land. He also observed a lower cadmium concentration in intensively (up to 30 cm depth) farmed and irrigated vegetable plots due to cadmium dilution (i.e mixing with low-Cd subsoil) with increasing depth

variation. Dilution of cadmium due to tillage practices on agricultural soil is the basis of the definitive strategy for soil sampling proposed under the TFMS in New Zealand (Stafford, A – Personal communication, September 2, 2015).

## **2.6. Heavy metal management in New Zealand**

A series of documents that suggest the development of soil guideline values for the management of contaminated land exists in New Zealand at both national and regional levels (Cavanagh, 2006a). A soil guideline value is the concentration of contaminant in soil that provides a safe window for the protection of human health and ecological receptors (Cavanagh, 2006a). The document list below represents the national documents containing soil guideline values applied for the management of contaminated land in New Zealand (Cavanagh, 2006a).

- *Health and Environmental Guidelines for selected Timber Treatment Chemicals (now referred to as the Timber Treatment Guideline) (MfE & MoH, 1997);*
- *Guidelines for Assessing and Managing Contaminated Gasworks Sites in New Zealand (now referred to as the Gasworks Guidelines) (MfE, 1997);*
- *Guidelines for Assessing and Managing Petroleum Hydrocarbon Industry Sites in New Zealand (now referred to as the Petroleum Hydrocarbon Guidelines) (MfE, 1999);*
- *Health Investigation Levels for Dioxin Contaminated Soil. Report for the Ministry for the Environment (Salcor, 2003);*
- *Assessing and Managing Risks Associated with Former Sheep-dip Sites: A guide for local authorities (now referred to as the Sheep-dip Guidelines) (MfE, 2006);*
- *National Environmental Standard (NES) for Contaminated Land: Notes of Technical Review Workshop (MfE, 2005);*

- *Guidelines for the Safe Application of Biosolids to Land in New Zealand (now referred to as the Biosolids Guidelines) (NZWWA, 2003);*
- *Module 2 – Hazardous Waste Guidelines – Landfill Waste Acceptance Criteria and Landfill Classification (MfE, 2004).*

Among the list of documents above, NES and biosolids guidelines relate more to the scope of this study and will be discussed here. NES was developed for the protection of human health from an array of exposure points (Cavanagh, 2006a). NES guidelines are based on an upgraded version of the Timber Treatment Guideline methodology for five exposure scenarios, including agricultural/horticultural land, residential (10%, 50% produce consumption), industrial (paved, unpaved) and sub-surface maintenance workers (Cavanagh, 2006a). Biosolids guidelines, on the other hand, were not primarily created for the management of contaminated land but they can be applied to contaminated lands or in the management of contaminated soil disposal (Cavanagh, 2006a). Biosolid guidelines were also created to assist in the application of biosolids to agricultural land and they involve soil limits (Cavanagh, 2006a). The soil limits show the maximum permissible concentration in the receptive environment for a varied number of metal and metalloid contaminants (Table 15) (Cavanagh, 2006a). These limits are typically based on the lowest contaminant concentration that supports protection of human health or ecological receptors (Cavanagh, 2006a). These two guidelines have been recommended for the management of contaminants from waste application to agricultural lands (MPI, 2015). Soil limits from NES and Biosolids guidelines applied for the management of metal contamination in New Zealand agricultural land is defined further in the next section.

### **2.6.1. New Zealand soil quality and food safety guidelines**

The Ministry for Primary Industries (MPI) has released guidelines to guide food producers and processors on best practices to ensure food safety and animal welfare from land application of waste (Cavanagh, 2015). Protection of soil biota and human health covered by the Biosolids Guidelines has been employed for monitoring heavy metal accumulation in landfarm-impacted soil in New Zealand (Cavanagh, 2015). In addition, National Environmental Standards for assessing and managing soil contaminants for the protection of human health provides the most current guideline for the protection of human health in a rural-residential land use scenario (Cavanagh, 2015). These two guideline standards (Table 15) are used to ensure safe application of drilling mud waste to land in New Zealand (Cavanagh, 2015). Since there is no soil guideline value for barite accumulation in New Zealand, the Alberta Environmental (2009) guideline is employed for protecting soil organisms from this contaminant and to manage any environmental implications of barium accumulation in landfarm-impacted soil.

**Table 15:** Suggested soil quality guidelines for safe application of oil and gas waste to land (Cavanagh, 2015)

Element	Biosolids soil limit <sup>1</sup> (mg/kg)	SCS-rural residential <sup>2</sup> (mg/kg)	Alberta Environmental (2009)
As	20	17	
Barium barite	–		10,000
Extractable barium			250
Cd	1	0.8	
Cr	600	No limit	
Cu	100	No limit	
Pb	300	160	
Ni	60	-	
Hg	1	200	
Zn	300	-	

<sup>1</sup>NZWWA (2003) - Lowest limit for human and ecological receptor protection; <sup>2</sup>MfE (2011).

Cadmium management in New Zealand has gained public sector interest due to its occurrence in phosphate fertiliser used for primary production (MAF, 2011). International and national risk-based guidelines have been used to formulate trigger values that can be applied for cadmium management in New Zealand agricultural land (MAF, 2011). Cadmium management and its trigger values specific to New Zealand will be explored further in the next section.

### 2.6.2. Cadmium regulation in New Zealand

Although tillage/continuous cultivation, plant uptake and organic matter/clay mineral sorption dilutes, removes or locks up soil cadmium, exposure pathways (soil ingestion, crop uptake etc) still predispose humans and animals to harmful effects and the most

essential means of reducing these impacts is by removing the source of the metal (Kirkham, 2006). However, limited availability of low cadmium-containing phosphate fertilizer and an absence of commercially feasible ways of abstracting cadmium from rock phosphate (and soil) means that cadmium will continue to accumulate in New Zealand soils (MAF, 2011).

In reaction to the likelihood of continued cadmium accumulation in New Zealand soil, the Chief Executive Environmental Forum established the Cadmium Working Group (CWG) backed by the Ministry of Agriculture and Forestry (now Ministry of Primary Industry) and tasked this group with the responsibility of evaluating possible risks relating to cadmium in New Zealand's agriculture and food systems (MAF, 2011). Stakeholders of CWG (now called Cadmium Management Group) are the rural production and environmental management representatives of the following groups (MAF, 2011);

- Meat and Wool New Zealand,
- Dairy Industry,
- Arable Food Industry Council,
- Horticulture New Zealand,
- Fertiliser Industry,
- Regional Councils,
- New Zealand Food Safety Authority,
- Ministry of Agriculture and Forestry (MAF) (Ministry for Primary Industries).

#### **2.6.2.1. Cadmium management strategy**

CWG assessed the New Zealand agricultural system and identified issues with cadmium contamination and the likely risks to human health, trade, economy and adaptability of

land to use change (MAF, 2011). Their report claimed that there is a minimal risk of exceeding food standards for cadmium in animal offal and vegetables with New Zealand. However, any exceedance of guideline values in food could result in erosion of our relationship with trade partners and loss of the country's clean green prestige. CWG also identified a potential risk in the adaptability of land to varied uses (residential or rural uses) due to cadmium accumulation (MAF, 2011). This assessment led to the recommendation of a risk-based strategy for cadmium management in New Zealand (MAF, 2011). The risk-based strategy is aimed at ensuring minimal risk to health, trade, land use adaptability and environment over the next 100 years (MAF, 2011). The strategy consists of two extensive and coinciding core areas; firstly, overall food monitoring programmes that will identify risks to trade and human health and secondly, a soil, water, fertiliser monitoring and fertilizer management programme which will provide a basic means of addressing the varied land use adaptability and environmental risks (MAF, 2011). Food, soil, fertiliser monitoring strategies is discussed further in Appendix 2. The following section focusses on a fertilizer management programme (TFMS) that addresses potential risk of cadmium accumulation with increasing fertiliser use.

#### **2.6.2.2. Tiered Fertiliser Management System (TFMS)**

TFMS is a New Zealand fertiliser industry initiative approved and adopted by the CWG as a desirable means of controlling cadmium accumulation in agricultural soil (Sneath, 2015). It is a central part of Cadmium Management Strategy (launched in 2011) that is now being administered by the Cadmium Management Group (Sneath, 2015; MAF, 2011). TFMS assists primary industry with a self-managing framework that ensures management of soil cadmium accumulation over a term of up to 100 years (Stafford et

al., 2014). The TFMS is a valuable system that promotes management of soil cadmium accumulation to land owners in New Zealand (MAF, 2011).

TFMS aims to reduce cadmium (Cd) accumulation in soil by imposing strict fertilizer management actions as Cd concentration increases above critical values where restrictions are placed on cadmium accumulation without the need for site-specific risk investigations (Stafford et al., 2014; MAF, 2011; Sneath, 2015).

#### ***2.6.2.2.1. TFMS trigger value formulation***

Trigger values for the TFMS were formulated from both New Zealand and international soil guideline values (MAF, 2011). The trigger values were developed based on specific risk-based soil guidelines and principles of hierarchy. The selection of guideline values using a risk-based assessment methodology is in preference to threshold values (MAF, 2011). The rationale for the selection of New Zealand soil guidelines is supported by this country's international reputation and the acceptability of such an approach by both national and local government and industry (MAF, 2011). A hierarchy of documents utilised in the formulation of trigger values in the tiered fertiliser management is shown in appendix 5.

The TFMS covers five Cd tiers (Table 16) differentiated by four soil cadmium concentration trigger values (MAF, 2011). The soil trigger values used in the TFMS are provisional values which aim to protect different endpoints (human health, ecological receptors, food safety standards and trade and groundwater) of concern in New Zealand (MPI, 2012). At tier 1 – 4 different and specific management activities and some level of restrictions are placed to minimise cadmium accumulation (Table 16) except at tier 0 where five-yearly screening soil test for cadmium level is required (Stafford et al.,

2014). The TFMS covers farms with historical or present phosphate fertiliser application at a rate 30 kg/ha/yr or above (Sneath, 2015).

**Table 16:** Tiered Fertilizer Management System and Trigger values (MAF, 2011; Sneath, 2015, MPI, 2012)

Tier	Management action required	Cadmium concentration (mg/kg)	Trigger value (mg/kg)	Sources of value
0	Five-yearly screening soil test for cadmium status	0–0.6		
1	Restricted application of certain products (fertilizer) to minimise accumulation, while landholders are required to test for cadmium every 5 years using approved programmes	>0.6–1.0	0.6	99 <sup>th</sup> percentile of natural background concentrations in Taylor et al (2007)
2	Application rates are further managed by use of a cadmium balance programme to ensure that cadmium does not exceed an acceptable threshold within the next 50 years	>1.0–1.4	1.0	NZ Biosolids guidelines (NZWWA, 2003)
3	Application rates are further managed by use of a cadmium balance programme to ensure that cadmium does not exceed an acceptable threshold within the next 50 years	>1.4–1.8	1.4	Canadian SQG (human and ecological ) for agricultural land use (CCME <sup>13</sup> , 1999)
4	No further accumulation above the trigger value	>1.8	1.8	UK Soil Guideline Value for allotments (Environment Agency, 2009).

#### 2.6.2.2.2. TFMS implementation and monitoring

The TFMS was launched by the fertilizer industry in 2011 with training and documentation of field staff and farmers while the actual sampling of farmers plots (organised by (Fertiliser Association of New Zealand member companies – Balance

<sup>13</sup> Canadian Council for Ministers for the Environment

Agri-Nutrients and Ravensdown) started in 2012 (Stafford et al., 2014). Implementation of the TFMS involves various processes outlined in table 17.

**Table 17:** TFMS Implementation process (Stafford et al., 2014)

<i>Preliminary stage</i>	Farmers and field officers training by the fertiliser industry; and discussion with farmers to gain farmer's trust and consent.
<i>First stage</i>	Soil screening involving field soil sampling and laboratory analysis by the fertiliser industry representatives. Soil sampling at this stage is maintained at 75 mm (top-soil) to minimise cost for farmers and identify the farm tier stage.
<i>Second stage</i>	Definitive soil sampling: This is only carried out for farms identified to be above tier 0 (1.0 mg/kg Cd). At this stage, soil sampling is taken from 150mm depth.
<i>Reporting</i>	The state of assessed farms is reported by the fertiliser industry and submitted to the Cadmium Working Group.

The fertilizer industry monitors cadmium levels in farmland through the different stages of sampling and laboratory testing using a cost effective means of testing soil to encourage farmer's participation in the TFMS (Stafford, A. – Personal Communication, September 2, 2015). The cost effective approach undertaken by the fertilizer industry (Balance Agri-Nutrients) is such that farmland are screened at a lower depth (0 – 7.5 cm) to determine the tier stage of the farmland (Stafford, A. – Personal communication,

September 2, 2015). However, farmland that reports a soil Cd concentration above 1.0 mg/kg (Tier 2) will then be followed up with definitive sampling to 15cm (Stafford et al., 2014; Stafford, A – Personal Communication, September 2, 2015). The soil Cd concentration at the definitive sampling depth (deeper soil layer sampling) may be lower than the screening stage due to the dilution effect of land management practices (tillage soil distribution) and this justifies the approach of the fertiliser industry to the initial top soil screening (Stafford et al., 2014; Stafford, A – Personal communication, September 2, 2015).

## **Chapter 3 : Methodology**

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### **3.1. Introduction**

This study is a synthesis of two greenhouse experiments that have as a common denominator, heavy metal accumulation in New Zealand agricultural soil. The first project assessed cadmium accumulation in leafy vegetables (spinach, silverbeet and lettuce) grown on two New Zealand commercial horticultural soils while the second project focused on heavy metal accumulation in pasture (ryegrass) and a cash crop (hemp) grown on agricultural soil that had been amended with drilling waste. Horticultural and impacted soils are the terms used in this work to categorise the individual projects aimed at assessing potential risk to relevant endpoints in New Zealand.

In this chapter, the description of soil treatments applied in this study is made, followed by a description of the plants used and the experimental design. Methods applied for plant harvest, soil sampling, laboratory preparation/analysis and data analyses using statistical methods are discussed.

### **3.2. Study area and sample description**

#### **3.2.1. Soil sample description**

Bulk composite soil samples used for the glasshouse trials (at the Plant Growth Unit (PGU), Massey University Palmerston North New Zealand) were collected from commercial vegetable farms in two locations (Pukekohe and Gisborne) and from a landfarm-impacted site in the Taranaki region. Pukekohe soil is a volcanic soil containing a significant concentration of allophane (a clay mineral with the potential to adsorb metals to soil surfaces) while the Gisborne soil is a recent soil with lower allophane content. Field notes recorded during soil sampling described Gisborne soil as

one with sandy and orange mottles lenses reflecting inputs of the Waimihia tephra deposited about 3300 years BP.

The bulk soil samples were mixed with a spade, then potted into replicate pots, each containing 4kg of soil. The drilling waste soil treatments are described in Table 18. Soil to waste ratio for the representative landfarm-impacted soil (Table 18) was formulated to represent the practical rate of application in Taranaki region. Four treatments were used to assess the relative impact of oil and gas waste on pastoral systems, while soil samples from Pukekohe and Gisborne were used for the evaluation of cadmium risks in horticultural soils.

**Table 18:** Drilling waste origin and description

<b>Treatments</b>	<b>Description</b>
<b>100% drilling waste</b>	Hydrocarbon rich oil waste obtained from an oil exploration site.
<b>50:50 mix of drilling waste/control soil</b>	6 kg drilling waste was mixed with 6 kg control (uncontaminated) soil
<b>Landfarm-impacted soil</b>	12 kg control soil was mixed with 33kg drilling waste excavated from a poorly-mixed subsurface soil horizon at a landfarm site.
<b>Control soil</b>	Uncontaminated soil adjacent to a landfarm site.

### **3.2.2. Plant description**

Lettuce, spinach and silverbeet (*Beta Vulgaris Fordhook green*) were seeded on the Pukekohe and Gisborne soils while hemp (*Cannabis sativa L*) and ryegrass (*Lolium perenne L*) were seeded on the excavated landfarm, 100% drilling waste and 50:50mix of drilling waste/control soil and a control soil. Lettuce and silverbeet were provided by

Landcare research, silverbeet was purchased from a New World supermarket, while hemp and ryegrass were provided by Chris Anderson (Massey University).

### **3.2.3. Experimental design and glasshouse trial**

A pot with dimensions of 16.5 x 16.5 x 19cm was used for the glasshouse trial. Five replicate pots were prepared for each of lettuce, spinach, silverbeet and a non-planted control for Pukekohe soil while for the Gisborne soil, six replicate pots were prepared for each of lettuce, spinach, silverbeet and a non-planted control. This was because more Gisborne soil than Pukekohe soil was provided for the trial. Pots were seeded with one (1) lettuce seed, fifteen (15) spinach seeds or ten (10) silverbeet seeds.

A single pot containing 4kg 100% drilling waste was used for each of hemp, ryegrass and a non-planted control. Similarly a single pot containing 4kg 50:50mix of drilling waste/control was used for hemp, ryegrass and a non-planted control. These pots containing 100% drilling waste and 50:50mix of drilling waste/control were not replicated due to limited quantity of the drilling waste provided. The landfarm-impacted and control treatments were replicated. Three replicate pots each containing 5kg of landfarm-impacted soil were used for hemp, ryegrass and a non-planted control. Three replicate pots each containing 5kg control soil were also used for hemp, ryegrass and non-planted control. In all cases the non-planted control treatment was used as a control sample to assess changes occurring in the planted treatments relative to undisturbed soil conditions. Pots were seeded with hemp (*Cannabis sativa L*) and ryegrass (*Lolium perenne L*). Each hemp replicate pot was seeded with ten (10) hemp seeds while ryegrass replicate pots received fifteen (15) seeds in all treatment pots. No fertiliser was applied to any treatment. All pots were hand watered at 80% field capacity to ensure plant growth.

### 3.2.4. Plant harvest and soil sampling

*First stage:* All replicate pots for baby spinach and silverbeet were thinned 36 days after seeding. At this time, half of the viable plants in relevant pots were removed. Soil samples from the thinned pots were collected using a small soil corer (internal diameter 1 cm) at the time of thinning. A visual record of plant development at the time of thinning is presented as Figure 2.



**(A) PUKEKOHE SOIL**



### **(B) GISBORNE SOIL**

**Figure 2:** Different plant response at stage one. Replicate pots are visible for lettuce on the top row, spinach on the middle row and silverbeet on the bottom row. Extent of growth at the time of thinning was greater for the Pukekohe soil (A) than for the Gisborne soil (B).

**Final stage:** Lettuce, spinach and silverbeet were harvested for all treatment replicates and three replicate soil samples were collected from random pots within each treatment (lettuce, spinach and silverbeet) for both Pukekohe and Gisborne soil pots using a corer (internal diameter 1 cm) 22 days after first stage harvest or 58 days after planting. A visual record of plant development at the time of final harvest is presented as Figure 3.



**(A) PUKEKOHE SOIL**



**(B) GISBORNE SOIL**

**Figure 3:** Plant response image at final stage. Replicates in this image follow columns in the order silverbeet, spinach and lettuce (from left to right) for the Pukekohe soil (A), and lettuce, spinach, silverbeet (left to right) for the Gisborne soil (B). Note: extent of plant development at final harvest was less for the Pukekohe soil. The reason for the reduction in growth rate for this soil relative to the Gisborne soil and to plant development at the thinning time is unknown.

**Hemp and Ryegrass:** Hemp and ryegrass were harvested from all treatment at 54 days after planting and a visual observation (Figure 4, 5, 6, 7) of the plants were recorded at harvest to depict the extent of plant growth. Hemp and ryegrass showed a similar growth response on landfarm-impacted and control soil (Figure 4 and 5). However, there was no appreciable plant (hemp and ryegrass) growth in 100% Drilling waste or the 50:50mix of drilling waste and control soil.

Soil samples for each replicate pot were collected using a 1 cm diameter soil corer at the time of plant harvest. Five soil samples were subsequently collected from each pot 70 days after initial plant harvest and kept at 3° C in a sterile plastic bag for dehydrogenase analysis. Contamination of plants by soil samples was avoided at harvest by careful harvesting and by washing the biomass with deionised water.



**Figure 4:** Hemp (right end column), Ryegrass (middle column) and control (without plant - left end column) response on control soil. Hemp and ryegrass show good response and dry matter growth on control soil.



**Figure 5:** Hemp (right end column), ryegrass (middle column) and control (without plant – left end column) on landfarm-impacted soil. Growth performance of hemp and rye grass on this treatment sample was good with appreciable biomass produced.



**Figure 6:** Hemp (right end column), ryegrass (middle column) and control (without plant – left end column) on the 100% drilling waste. Hemp and ryegrass response to Drilling waste was poor.



**Figure 7:** Hemp (right end column), ryegrass (middle column) and control (without plant – left end column) on the 50:50 mix of drilling waste and control soil. There was poor hemp and ryegrass growth in this treatment but was better than the 100% drilling waste.

Harvested plants and soil samples were taken to Massey University's Soil and Earth Science analytical laboratory for further analysis of heavy metal concentration and dehydrogenase activity.

### **3.3. Laboratory analysis**

#### **3.3.1. Sample preparation**

Plant samples were rinsed with deionised water immediately after harvest, then oven dried (60-70<sup>0</sup>C) for three days to attain constant weight. The fresh weight and dry weight of final harvest replicates of lettuce, spinach and silverbeet was recorded. Dry plant samples were crushed in paper bags. Soil samples were air dried at 30 – 40<sup>0</sup>C for three days and then passed through <2 mm sieve prior to laboratory analysis. The sieved

soil samples and crushed plant samples were stored in closed plastic containers prior to acid digestion.

### **3.3.2. Acid digestion**

0.1 g of crushed plant samples and 1 g sieved soil samples were each weighed into glass digestion tubes, and pre-digested with 10 ml 70% nitric acid overnight. The following day, digest preparations were heated at 120<sup>0</sup>C for 3hours, the temperature was raised to 135<sup>0</sup>C for 30 minutes, and then raised to 140<sup>0</sup>C for 2hours 30minutes. This procedure resulted in complete digestion of plant material. After digestion, all samples were cool for 15 minutes and then diluted to 25 mL with deionised water, mixed using a vortex mixer (10 seconds) and filtered through Whatman 42 filter papers.

### **3.3.3. Soil extraction**

A subset of soil samples was extracted with 0.1 M CaCl<sub>2</sub> at a soil: solution ratio of 1:5 (5 g soil to 25 mL solution) using overnight extraction on an end-over-end shaker to estimate the bioavailable concentration of Cd in soil. The acid oxalate–extractable Fe and Al concentration in these same samples was quantified following the methods described by Blackmore et al. (1987). The oxalate extractable Fe and Al technique attempts to quantify allophane content: ammonium oxalate extraction will target amorphous Fe and Al and is a proxy for allophane content. In brief, soils were extracted using 0.02 M ammonium oxalate buffered to pH 3.25 with oxalic acid. Extraction was performed at a 1:10 soil to solution ratio for over 4 hours (in darkness).

### **3.3.4. Elemental analysis**

The quantification of the Cd concentration in each digest solution and relevant extract was performed using graphite furnace atomic absorption spectroscopy (GFAAS) using a Perkin Elmer AAnalyst600. The method detection level for cadmium was 10 ng/L. This

corresponded to a minimum detectable Cd concentration in soil of 15 ng/g (ppb) and a minimum Cd concentration in plants of 150 ng/g dry weight (ppb).

The quantification of other heavy metals (Zinc, Nickel, and Copper) in each digest was performed using MP-AES (Microwave Plasma 4200 AES, Agilent Technologies). The Al/Fe concentration in extract solution was determined by MP- AES. The method detection limit for other metals in MP-AES was 0.1 mg/kg (ppm) which corresponds to 0.15 mg/kg (ppm) in soil and 1.5 mg/kg (ppm) in plant.

### **3.3.5. Dehydrogenase activity**

Microbial oxidation of organic compounds is directly associated with electron transport chain (ETC) that uses oxygen as a final electron acceptor (Gregory et al., 2015). Dehydrogenases are essential enzymes that form a critical part of microbial ETC and can be measured experimentally using artificial electron acceptors like tetrazolium (TTC) salts (Gregory et al., 2015). A 5 g sample of fresh soil was mixed with 3 ml of 3% 2, 3, 5 – triphenyl-tetrazolium chloride (3% TTC) and 0.1 g calcium carbonate and incubated for 24 hours at 28°C (Chander & Brooke, 1991). The triphenylformazan (TPF) formed in the reaction was extracted with methanol and its concentration quantified by measuring the absorbance in a JENWAY 7315 spectrophotometer at 485 nm. Microbial activity is proportional to the intensity of absorbance (Jeyakumar et al., 2010). Fresh soil samples (5g) were oven dried overnight at 105°C to determine the moisture content of the soil at harvest. Jeyakumar et al. (2008) set dehydrogenase activity for uncontaminated soil at 100% which is then applied to determine changes in contaminated soil.

### **3.3.6. Quality control**

Analytical blank samples were included in each digestion series. The concentration of Cd in each blank solution was below the limit of detection. The accuracy of analysis was assessed using a plant standard reference material (SRM: Tomato leaves). The digestion protocol used for the SRM was the same as for trial samples. Recovery of cadmium from the standard reference material was between 74-85%, within the acceptable range for this sample. The recovery of Zn from the standard reference material was greater than 80% while Ni, Co and Cu recovery was within 103%. Absorbance reading for the dehydrogenase enzyme activity in blank solution was below detection limit (0.000).

### **3.3.7. Soil fertility parameters**

Five replicate soil samples for lettuce grown on Pukekohe soil were separately sampled and mixed to form a composite sample. The same method was followed to generate a composite sample for silverbeet and spinach from the Pukekohe soil. Similarly, six replicates soil samples for each of lettuce, spinach and silverbeet grown on the Gisborne soil were collected and mixed to generate three composite soil samples. These three composite samples from each of the two soils were analysed for standard soil fertility parameters by Hill Laboratories, and for C and N at Massey University.

## **3.4. Statistical analysis**

Minitab® version 17 statistical software was employed for the statistical analysis. Descriptive statistics (Mean and standard deviation) was performed for the respective treatments. However, this was not conducted for treatments without replicates (100% drilling and 50:50mix drilling waste and control). Analysis of Variance was conducted using the Minitab® 17 (Minitab 17 Statistical Software, 2010) to determine whether there were significant differences (least significant difference at 5% probability level)

among the various treatment means. Turkey Pairwise comparison (95% confidence level) was used to group the significantly different means.

## **Chapter 4 : Results**

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### **4.1. Introduction**

In this Chapter, results from laboratory and data analysis are presented according to the following section: physical and chemical properties of all soil samples; heavy metal accumulation in all plants and soil treatments assessed; dehydrogenase activity in impacted soil; and hemp biomass in all impacted pot trials. The term horticultural soils and impacted soils used here is as defined in the previous chapter. These two soil ‘types’ were used to determine the heavy metal risks associated with the agricultural land use options in New Zealand that are the subject of this thesis.

### **4.2. Physical and Chemical properties of all soil samples**

The standard nutrient properties of all soil samples are summarised in Table 19.

#### **4.2.1. Horticultural soils**

##### **4.2.1.1. Pukekohe soil**

Pukekohe soil has a bulk density (0.98 g/mL) within the medium range for New Zealand agricultural soils. The soil has neutral pH level (6.7). The soil has high sulphate sulphur concentration (66 mg/kg), above the medium level (Table 19). The soil Olsen P value (81.33 mg/L) was also high. The Pukekohe soil has a cation exchange capacity in the medium range for NZ soils (17 me/100g), also has medium base saturation (79.67%). The soil has a high concentration of extractable cations (K – 1.51 me/100g; Ca - 10.80 me/100g) with the exception of sodium (Na – 0.35 me/100g) and magnesium (Mg – 0.89 me/100g) cation at medium and low levels respectively. The Pukekohe soil has low carbon (2.13%) and nitrogen (0.24%) content with a low C/N ratio (8.7).

#### **4.2.1.2. Gisborne soil**

The Gisborne soil has a bulk density (0.81 g/mL), base saturation (69%) and cation exchange capacity (21 me/100g) within medium ranges for agricultural soil (Table 19). The soil has a low pH value of 5.6. The Gisborne soil has sulphate sulphur concentration (18.67 mg/kg) and Olsen P value (49.67 mg/L), above medium ranges. The soil also has high extractable Ca (12.13 me/100g) and medium Mg (1.63 me/100g), K (0.51 me/100g) and Na (0.37 me/100g). The Gisborne soil has low carbon (2.17%) and nitrogen (0.25%) content and also has a low C/N ratio (8.6).

#### **4.2.2. Impacted soil treatments**

##### **4.2.2.1. 100% drilling waste**

100% drilling waste has a bulk density (0.98 g/mL) and base saturation (71%), within medium range for agricultural soil. The soil pH level (6.6) is slightly acidic with a sulphate sulphur concentration (75 mg/kg) in the high range. The soil has low CEC (11 me/100g) and Olsen P level (17 mg/L). Extractable cations in the 100% drilling waste were at medium levels (Ca – 4.9 me/100g; Mg – 1.05 me/100g; Na – 0.54 me/100g) with the exception of K (1.06 me/100g) which was present at high concentration.

##### **4.2.2.2. Landfarm-impacted soil**

The impacted soil had a high bulk density (1.55 g/mL) and slightly acidic pH level (6.6) that was in the high range for a New Zealand soil. The CEC (7 me/100g) and sulphate sulphur concentration (9 mg/kg) was low for pastoral soils. The landfarm-impacted soil had a high Olsen P value (42 mg/L) and base saturation (100%). Among the four extractable cations analysed, K (0.17 me/100g), Mg (0.53 me/100g) and Na (0.15 me/100g) was observed to be in the medium range, except for Ca (5.8 me/100g), which was medium.

#### **4.2.2.3. Control soil**

The control soil has a bulk density (1.59 g/mL) which is above the medium range. The soil has a mildly acidic pH (5.7) level and Olsen P value (21 mg/L) within medium range for pastoral soil while the CEC (7 me/100g), sulphate sulphur (9 mg/kg) and base saturation (40%) were all below medium range for pastoral soil. All the extractable cations (K – 0.07 me/100g; Ca – 2.0 me/100g; Mg – 0.62 me/100g) in control soil were below medium ranges except for Na (0.21 me/100g) that was at medium level.

**Table 19:** Physical and chemical Characteristics of horticultural and drilling waste impacted soil samples from different locations in New Zealand

Source	VW	pH	CEC	SO <sub>4</sub> -S	C	N	C/N	Olsen P	Base saturation	Extractable cation			
	g/mL		me/100g	mg/kg	%	%	Ratio	mg/L	%	me/100g			
										K	Ca	Mg	Na
<i>Pukekohe</i>	0.96	6.6	17	66	2.13	0.24	8.7	81.33	79.67	1.51	10.80	0.89	0.35
<i>Gisborne</i>	0.81	5.6	21	18.67	2.17	0.25	8.6	49.67	69	0.51	12.13	1.63	0.37
<i>100% drilling waste</i>	0.98	6.5	11	75	-	-	-	17	71	1.06	4.9	1.05	0.54
<i>Landfarm-impacted soil</i>	1.55	6.6	7	9	-	-	-	42	100	0.17	5.8	0.53	0.15
<i>Control soil</i>	1.59	5.7	7	9	-	-	-	21	40	0.07	2.0	0.62	0.21
<i>Medium ranges<sup>14</sup></i>	0.60 – 1.00	5.8 – 6.2	12 – 25	10 – 12	4 - 10	0.20 – 0.5	10 - 15	20 – 30	50 – 85	0.40 – 0.60	4.0 – 10	1.00 – 1.60	0.20 – 0.50

*Source: Authors laboratory result*

**VW** = Volume weight; **Composite** = Soil samples from hemp and ryegrass pot mixed together; **CEC** = Cation Exchange Capacity; **SO<sub>4</sub>-S** = Sulphate Sulphur; **K** = Potassium; **Ca** = Calcium; **Mg** = Magnesium; **Na** = Sodium; **C** = Organic carbon; **N** = Total Nitrogen; **H** = Total hydrogen; **S** = Organic sulphur.

<sup>14</sup> Hill Laboratory (no date)

### 4.3. Heavy metal accumulation in horticultural soils

#### 4.3.1. Total cadmium concentration in Pukekohe and Gisborne soil

The total Cd concentration in the Pukekohe soil was  $0.26 \pm 0.17$  mg Cd/kg soil and the total Cd concentration in the Gisborne soil was  $0.11 \pm 0.01$  mg Cd/kg soil. These values were significantly below soil quality guidelines for safe application of biosolids to land (Table 20). The Cd concentration in both horticultural soils was within the tier 0 trigger values for cadmium management in New Zealand and therefore no Cd management strategy is needed for these two soils (Table 16).

**Table 20:** Mean (and standard deviation) cadmium and zinc concentration in two different New Zealand commercial horticultural soils.

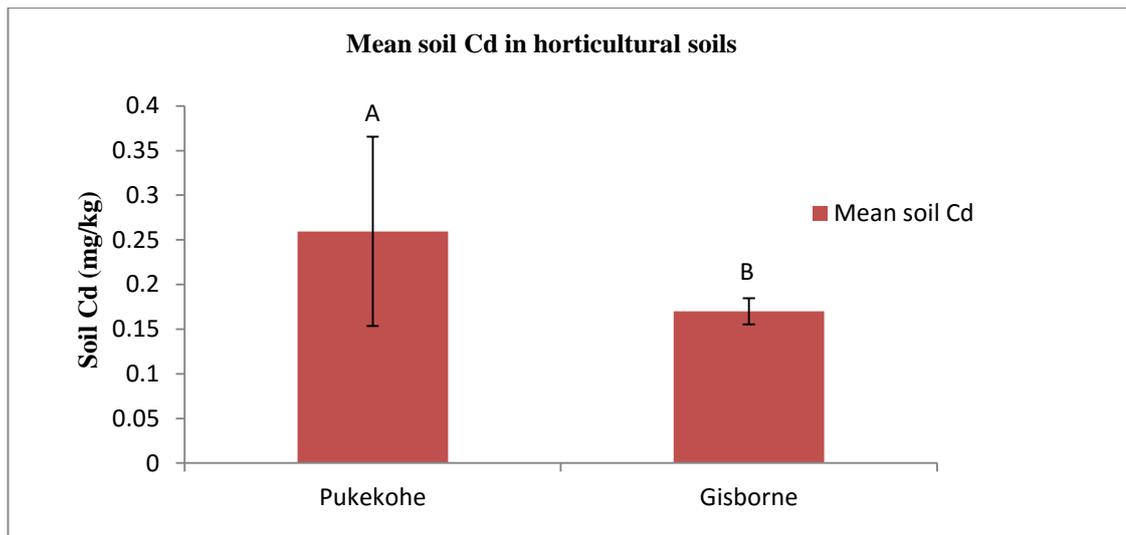
<i>Site location</i>	<b>Total cadmium (mg/kg)</b>		<b>Zn (mg/kg)</b>	
	<i>Pukekohe soil</i>	<i>Gisborne soil</i>	<i>Pukekohe soil</i>	<i>Gisborne soil</i>
<i>Soil Cd</i>	$0.26 \pm 0.17^A$	$0.11 \pm 0.01^B$	$130.34 \pm 17.74^A$	$69.63 \pm 6.07^B$
<i>Soil limit guideline (NZWWA, 2003)</i>	<b>1</b>		<b>300</b>	

*Source:* Authors laboratory result

Different alphabetical letters (A or B) suggests significant difference within the group at  $p < 0.05$  at the same stage of harvest.

#### 4.3.2. Comparison of total cadmium concentration in Pukekohe and Gisborne soil

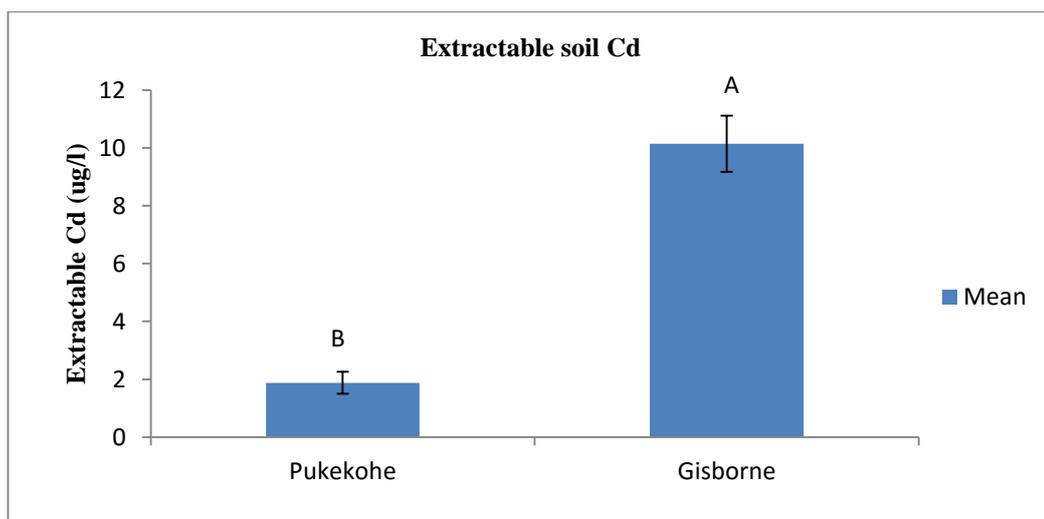
A direct comparison of the soil Cd concentration in the two horticultural soils (Gisborne and Pukekohe) is shown in Figure 8. The result of this study shows that soil Cd concentration in Pukekohe soil was significantly greater ( $P < 0.05$ ) than Gisborne soil (Figure 8).



**Figure 8:** Cadmium concentration (mg Cd/kg soil) in horticultural soils. Different letters are significantly differing within the group at  $p < 0.05$ .

#### 4.3.3. Extractable Soil Cadmium in Horticultural soils

The extractable Cd concentration in the Pukekohe and Gisborne soils was  $1.88 \pm 0.38$   $\mu\text{g Cd/L}$  and  $10.14 \pm 0.97$   $\mu\text{g Cd/L}$  soil solutions respectively. This result suggests a significantly greater ( $P < 0.05$ ) extractable Cd concentration in the Gisborne soil compared to the Pukekohe soil (Figure 9).



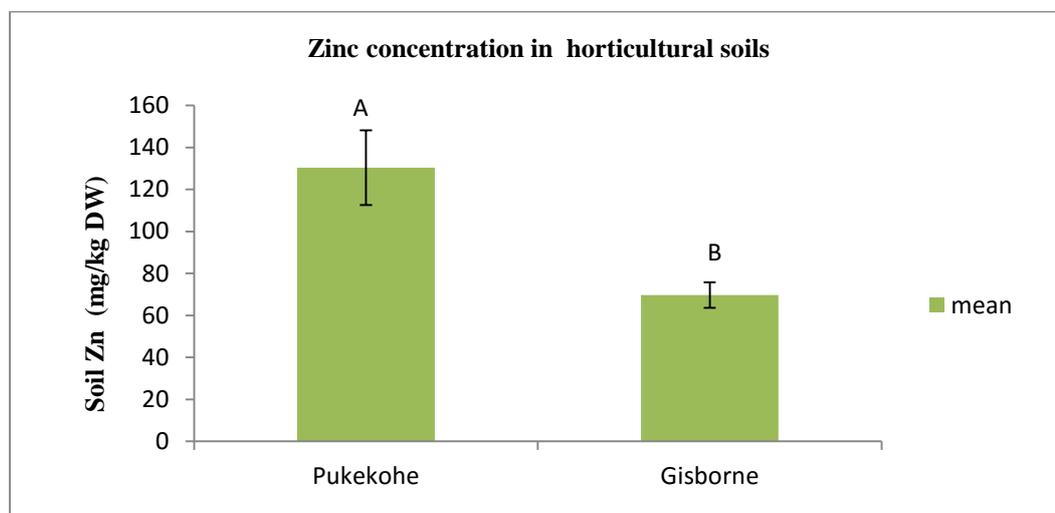
**Figure 9:** Concentration of extractable Cd determined through extraction at 1:5 soil to solution ratio (extractant is 0.05 M  $\text{CaCl}_2$ ). Different letters are significantly different ( $P < 0.05$ ) among treatments.

#### 4.3.4. Soil reactions influencing Cd Concentration

The total Zn concentration in soil and the oxalate extractable Fe and Al concentration in soil have been proposed as influencing parameters on Cd availability in soil. An assessment of these two parameters in the horticultural soils is presented here.

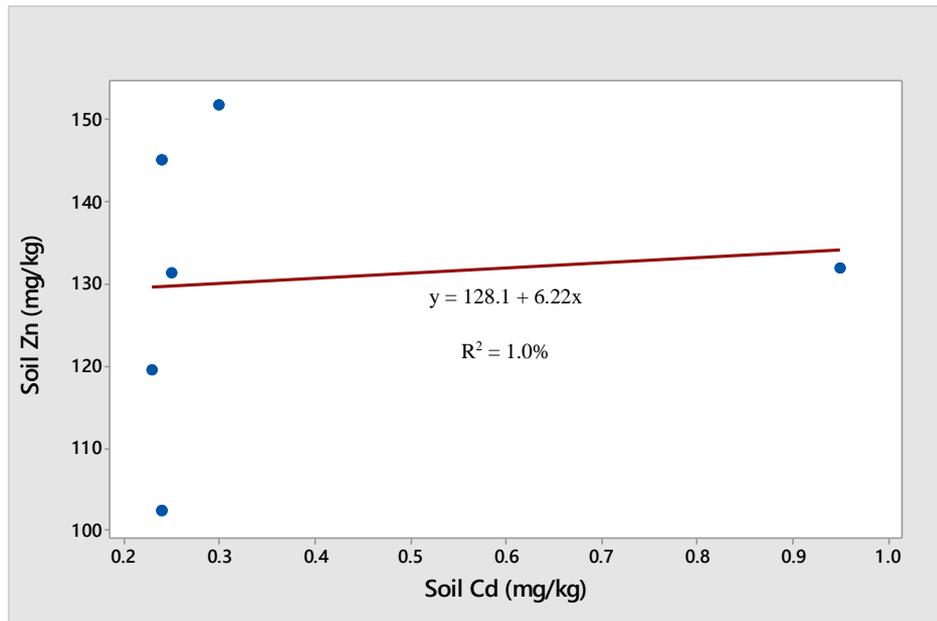
##### 4.3.4.1.1. Cd/Zinc interaction in horticultural soils

The total Cd and Zn concentration in the two soils is presented in table 20, with the comparison of Zn concentration graphically displayed in figure 10. There was a significant difference in the Zn concentration between the two soils: Pukekohe soil ( $130.34 \pm 17.74$  mg Zn/kg DW) and Gisborne soil ( $69.63 \pm 6.07$  mg Zn/kg DW). The Zn concentration in both soils was below the soil limit (300 mg Zn/kg WD) for bio-solid application (NZWWA, 2003).

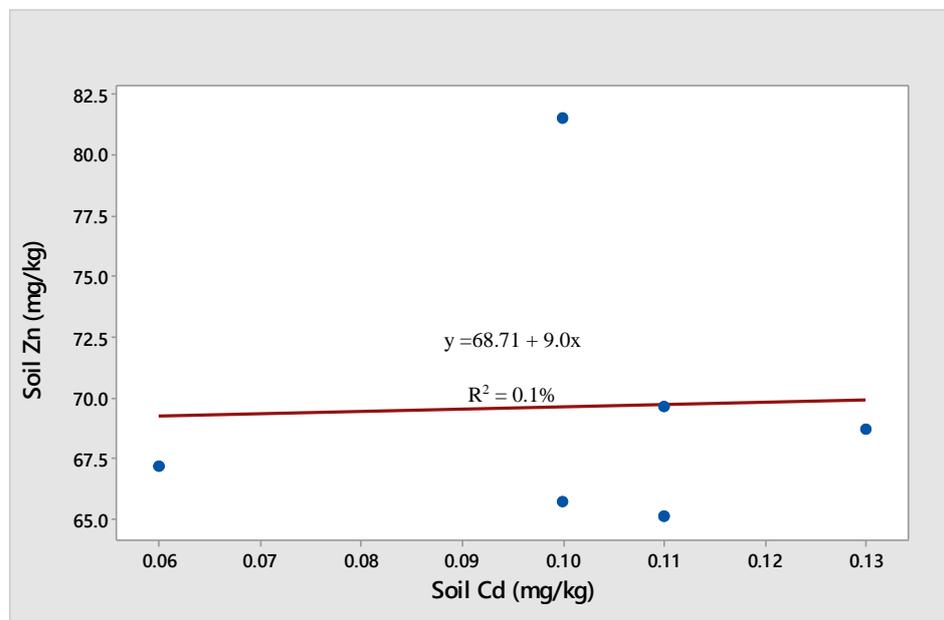


**Figure 10:** Zinc concentration (mg Zn/kg soil) in soils at the final harvest. Different letters are significantly differing within the group at  $p < 0.05$ .

The relationship between Cd/Zn concentrations in the two horticultural soils is shown in Figure 11. The correlation coefficients (R) for Cd/Zn relationship in the two horticultural soils were found to be insignificant and positive ( $P > 0.05$ ).



**(A) Pukekohe Soil**

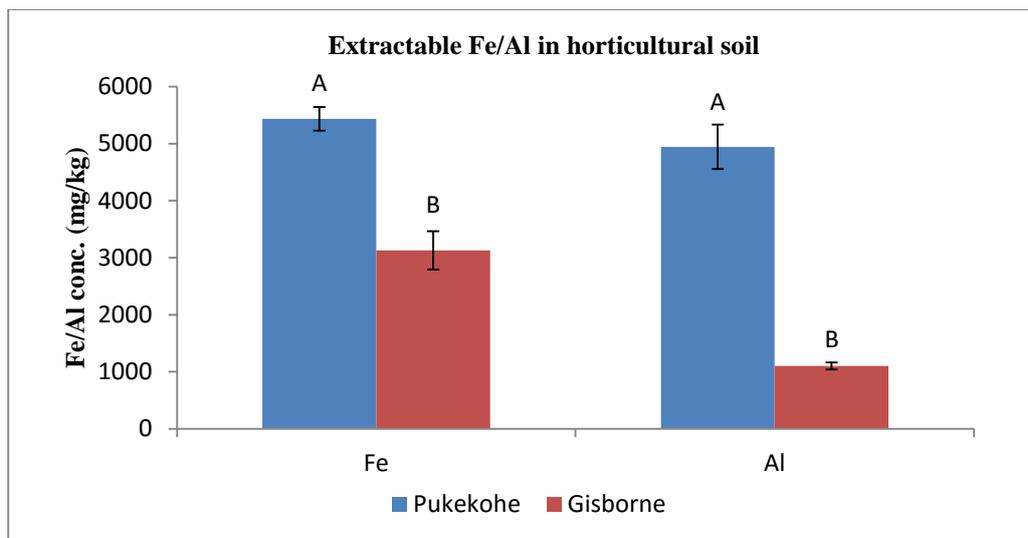


**(B) Gisborne Soil**

**Figure 11:** Relationship between total Zn and Cd concentration in Pukekohe soil (A) and Gisborne soil (B)

#### 4.3.4.1.2. Oxalate extractable Fe and Al in horticultural soils

The Extractable Fe and Al concentration for the two horticultural soils used in this study is presented in Figure 12. The extractable Fe and Al concentration is significantly lower for the Gisborne soil ( $3128 \pm 336$  mg Fe/kg and  $1102 \pm 61$  mg Al/kg) relative to the Pukekohe soil ( $5435 \pm 206$  mg Fe/kg and  $4943 \pm 388$  mg Al/kg). Our analysis demonstrates that the allophane content of the Pukekohe soil is higher of the two soils.



**Figure 12:** Comparison of oxalate extractable Al and Fe concentration in the two horticultural soils. Different letters shows significant difference ( $P < 0.05$ ) between the two soil samples.

### 4.4. Heavy metal concentration in impacted agricultural soil

The concentration of heavy metals analysed in this study (Zn, Cu, Cd and Ni) in the impacted agricultural soils experiment is shown in table 21.

#### 4.4.1. Heavy metal concentration in landfarm-impacted soil

The Cd Cu, Ni and Zn concentration in the landfarm-impacted soil was  $0.1 \pm 0.0$  mg Cd/kg;  $12.57 \pm 1.13$  mg Cu/kg; BDL and  $29.99 \pm 3.33$  mg Zn/kg respectively (Table 21). These concentrations were all within typical values for cultivated New Zealand

soil. They were also within soil quality guidelines for safe application of biosolids (Table 21).

#### **4.4.2. Heavy metal concentration in control soil**

The Cd ( $0.1 \pm 0.0$  mg/kg), Cu ( $11.5 \pm 2.44$  mg/kg), Zn ( $29.14 \pm 7.36$  mg/kg), and Ni (BDL) concentration in the control soil was also within typical ranges of values for New Zealand cultivated soil and soil quality guidelines for safe application of biosolids (Table 21).

#### **4.4.3. Heavy metal concentration in 100% drilling waste**

The Cd ( $0.1 \pm 0.0$  mg/kg), Zn (BDL), Cu ( $77.48 \pm 2.59$  mg/kg) and Ni (BDL) concentration in the 100% drilling waste was again within soil quality guidelines for the safe application of biosolids to land. The concentration was within typical values for New Zealand cultivated land with the exception of Cu (Table 21).

#### **4.4.4. Heavy metal accumulation in 50:50 mix of drilling waste/control soil**

The Zn ( $12.13 \pm 1.0$  mg/kg), Ni (BDL), Cu ( $45.93 \pm 12.02$  mg/kg) and Cd ( $0.1 \pm 0.0$  mg/kg) concentration in 50:50 mix drilling waste/control soil was within the soil quality guideline for safe application of biosolids to land (Table 21) and within typical New Zealand values for cultivated soils except Cu (Table 21).

**Table 21:** Heavy metal concentration on landfarm-impacted agricultural soil

Treatment	Cd (mg/kg)	Zn (mg/kg)	Cu (mg/kg)	Ni (mg/kg)
50:50% (Drilling waste/control)	0.1 ± 0.0 <sup>A</sup>	12.13 ± 1.0 <sup>B</sup>	45.93 ± 12.02 <sup>B</sup>	BDL
100% (Drilling waste)	0.1 ± 0.0 <sup>A</sup>	BDL	77.48 ± 2.59 <sup>A</sup>	BDL
Landfarm-impacted soil	0.1 ± 0.0 <sup>A</sup>	29.99 ± 3.33 <sup>A</sup>	12.57 ± 1.13 <sup>C</sup>	BDL
Control soil	0.1 ± 0.0 <sup>A</sup>	29.14 ± 7.36 <sup>A</sup>	11.5 ± 2.44 <sup>C</sup>	BDL
Typical value for farmed soil (Edmeades, 2013)	0.1 – 0.8	7 - 79	10 – 20	4 -14
Soil limit guideline (NZWWA, 2003)	1	300	100	60

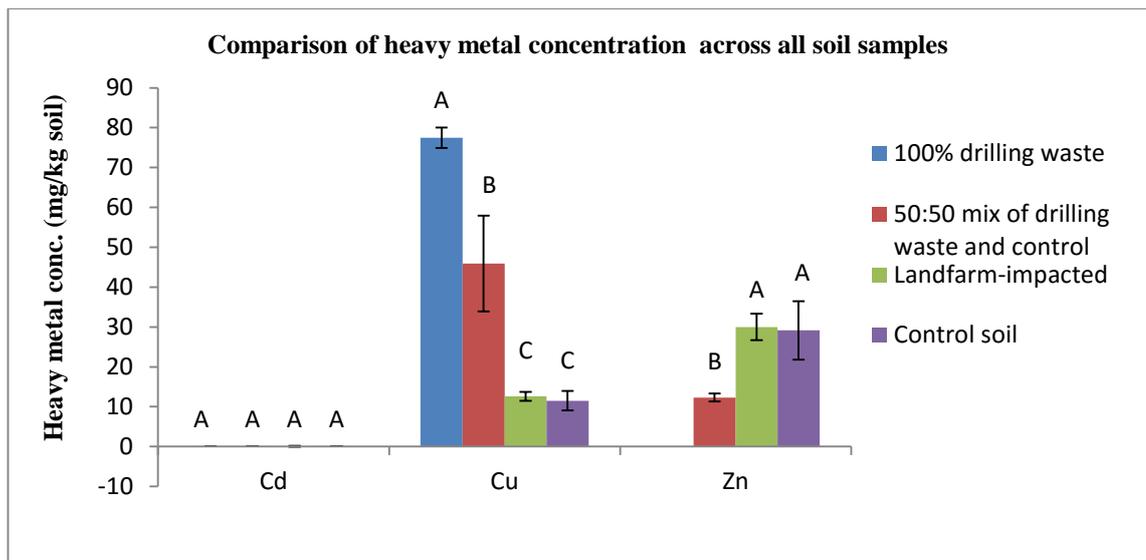
*Source: Authors Laboratory result*

*BDL – Below detection limit (0.1mg/kg).*

*Means of samples with same letters are not significantly different (P = 0.05) between plants for each metals. ng = not given*

#### 4.4.5. Comparison of heavy metal concentration across all soil treatments

There was no significant difference ( $P>0.05$ ) in the Cd concentration across all soil treatment (Figure 13). The concentration of Zn in landfarm-impacted soil and control soil was not significantly different ( $P>0.05$ ), but was different to the concentration in 50:50 mix of drilling waste/control soil (Figure 13). The Cu concentration was highest in 100% drilling waste and this concentration was significantly greater than for the other treatments ( $P>0.05$ ) (Figure 13). The Cu concentration in soil followed the trend: 100% drilling waste>50:50mix>landfarm-impacted soil and control. The Ni concentration in all soil treatments were below detection limit.

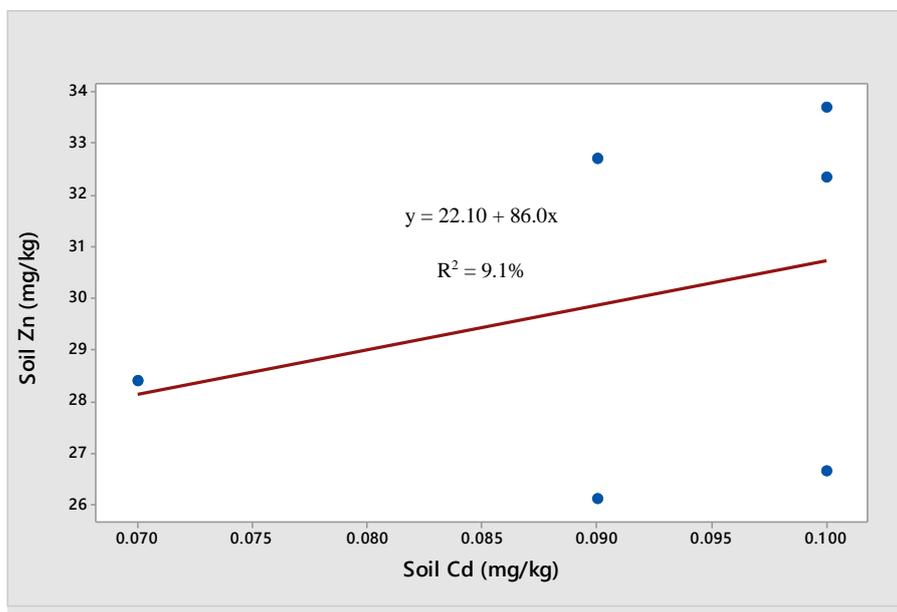


**Figure 13:** Comparison of heavy metal concentration in all soil treatments. Same Letters indicates no significant difference ( $P>0.05$ ) across soil treatments for a heavy metal.

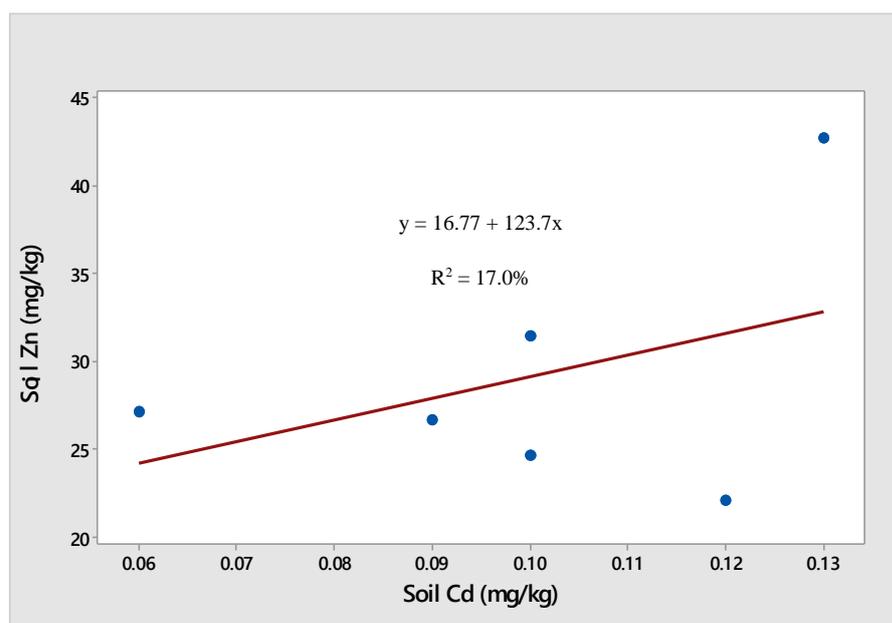
#### 4.4.6. Soil reaction influencing heavy metal behaviour in impacted soil

##### 4.4.6.1. Cd/Zn interaction in impacted soil

The correlation between Cd/Zn concentrations in landfarm-impacted soil and a control soil is shown in Figure 14. The correlation coefficients (R) for Cd/Zn relationship in the landfarm-impacted soil and a control soil were found to be insignificant and positive (P > 0.05).



(A) Landfarm-impacted soil



**(B) Control soil**

**Figure 14:** Relationship between Cd and Zn concentration in landfarm-impacted soil (A) and a control soil (B)

#### **4.5. Heavy metal concentration in leafy vegetables in horticultural soil at different growth stages**

##### **4.5.1. Cadmium concentration in leafy vegetables in Pukekohe soil**

**First stage:** The trend of relative Cd concentration between the three leafy vegetables was very similar (dry weight) and followed the order spinach > silverbeet > lettuce. The mean Cd concentration in first stage baby spinach ( $1.03 \pm 0.2$  mg/kg DW) was significantly greater ( $P < 0.05$ ) than in silverbeet ( $0.56 \pm 0.1$  mg/kg DW) for the Pukekohe soil harvested at the same time (Table 22). The Cd concentration in spinach and silverbeet exceeded the tolerable limit for agronomic crops at the first stage.

**Final stage:** The mean Cd concentration in baby spinach ( $1.11 \pm 0.1$  mg/kg DW) was also significantly greater ( $P < 0.05$ ) than in silverbeet ( $0.41 \pm 0.07$  mg/kg DW) and lettuce ( $0.16 \pm 0.02$  mg/kg DW) at final harvest. The Cd concentration in lettuce and

silverbeet was within tolerable limits in agronomic crops at final harvest; however the Cd concentration in spinach exceeded the limit.

**Fresh weight:** When expressed on a fresh weight basis, the average fresh weight Cd concentration in spinach ( $0.1 \pm 0.02$  mg/kg FW) was also significantly greater than in silverbeet ( $0.05 \pm 0.01$  mg/kg FW) and lettuce ( $0.02 \pm 0.00$  mg/kg FW) at final harvest. Lettuce and silverbeet showed a Cd concentration below CODEX (2010) and FSANZ (2011) maximum permissible limit for leafy vegetables while the Cd concentration in spinach was below CODEX (2010) but at FSANZ (2011) maximum permissible limits for leafy vegetables.

#### **4.5.2. Cadmium concentration in leafy vegetables in Gisborne soil**

**At first stage:** There was no significant difference ( $P > 0.05$ ) between the Cd concentration in spinach and silverbeet for the first-stage harvest from the Gisborne soil although the concentration in spinach was nominally higher (spinach  $1.61 \pm 0.3$  mg/kg and silverbeet  $1.22 \pm 0.2$  mg/kg). The Cd concentration in spinach and silverbeet in the Gisborne soil exceeded the tolerable limits for agronomic crops at the first stage.

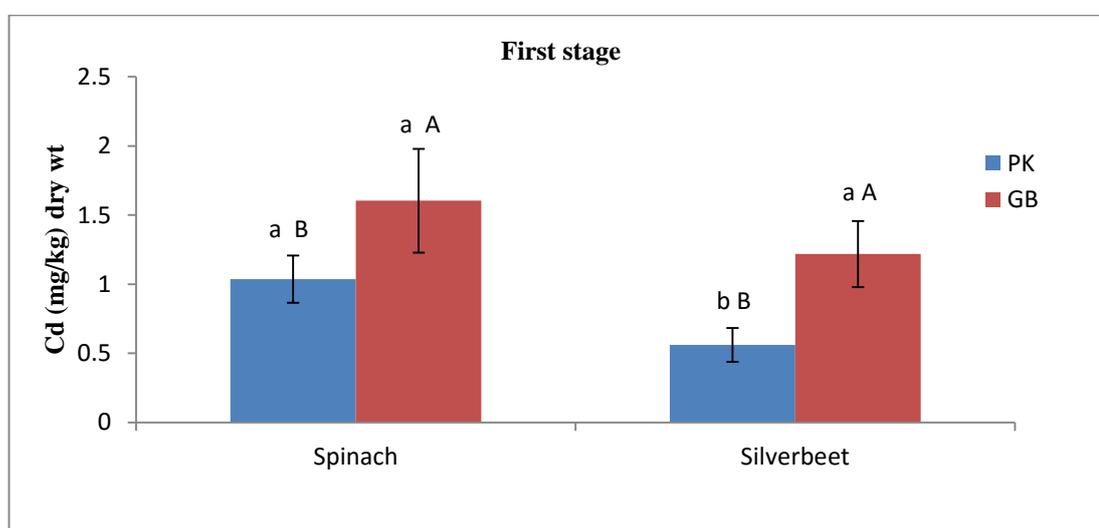
**At final stage:** The average Cd concentration in spinach ( $2.13 \pm 0.50$  mg/kg DW) was significantly greater than in silverbeet ( $0.93 \pm 0.26$  mg/kg DW) and lettuce ( $0.48 \pm 0.06$  mg/kg DW) at final harvest while there was no significant difference in the Cd concentration in silverbeet and lettuce ( $P > 0.05$ ). The Cd concentration in spinach, lettuce and silverbeet grown on Gisborne soil exceeded the tolerable limits for agronomic crops.

**Fresh weight:** The fresh weight Cd concentration in spinach ( $0.27 \pm 0.06$  mg/kg FW) and silverbeet ( $0.12 \pm 0.04$  mg/kg FW) exceeded CODEX (2010) and FSANZ (2011) maximum permissible limits for leafy vegetables, while the Cd concentration in lettuce

( $0.04 \pm 0.01$  mg/kg FW) was below FSANZ (2011) and CODEX (2010) maximum permissible limits for leafy vegetables.

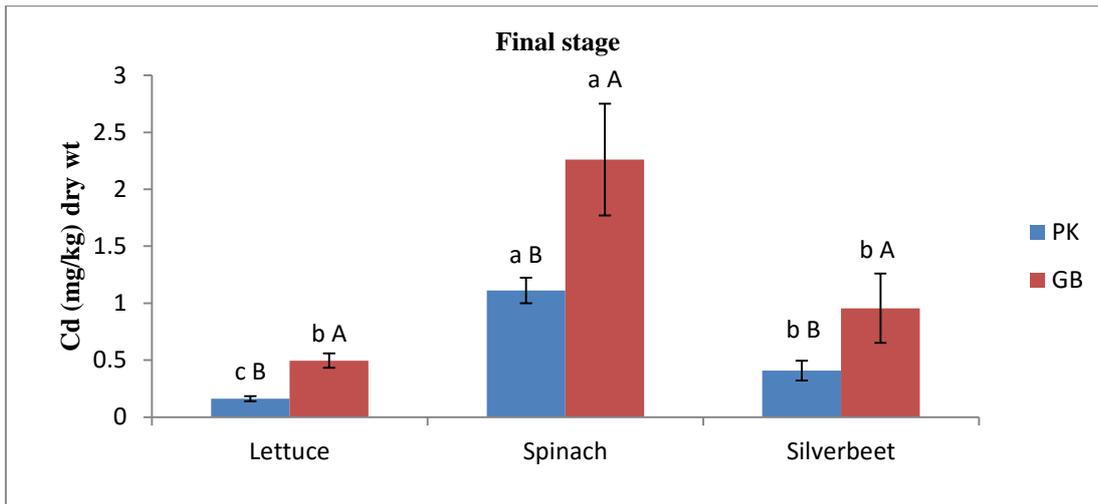
#### 4.5.3. Comparison of cadmium uptake in Pukekohe and Gisborne soil

The Cd concentration in baby spinach and silverbeet harvested from Gisborne and Pukekohe soil at thinning time (first stage) is presented in Figure 15. The Cd concentration in spinach and silverbeet was significantly higher ( $P < 0.05$ ) for the Gisborne soil relative to the Pukekohe soil at the first stage, despite the lower concentration of total Cd in the Gisborne soil.



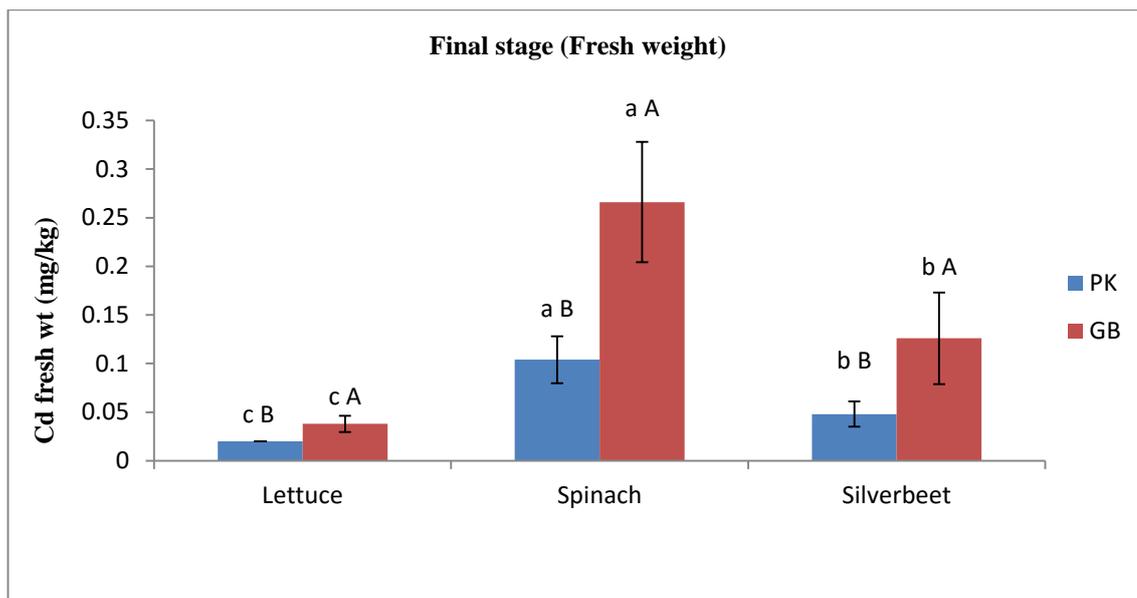
**Figure 15:** Cadmium concentration (mg/kg DM) in plants at first stage. (i) Capital letters indicate differences in cadmium concentration in plant species grown on different soil, and (ii) simple letters indicate differences in cadmium concentration for the different plant grown on the same soils. Means with the same letter are not significantly different ( $p = 0.05$ ). PK is the Pukekohe soil; GB is the Gisborne soil.

The dry weight Cd concentration in all three plant species at final harvest is presented in Figure 16. The mean Cd concentration in all three leafy vegetables (spinach, lettuce and silverbeet) was significantly greater when grown on Gisborne soil relative to the Pukekohe soil (Figure 16).



**Figure 16:** Cadmium concentration (mg/kg DM) in plants at final stage. (i) Capital letters indicate differences in cadmium concentration in plants species grown on the different soil, and (ii) simple letters indicate differences in cadmium concentration for the different plants grown on the same soils. Means with the same letter are not significantly different ( $p=0.05$ ). PK is the Pukekohe soil; GB is the Gisborne soil.

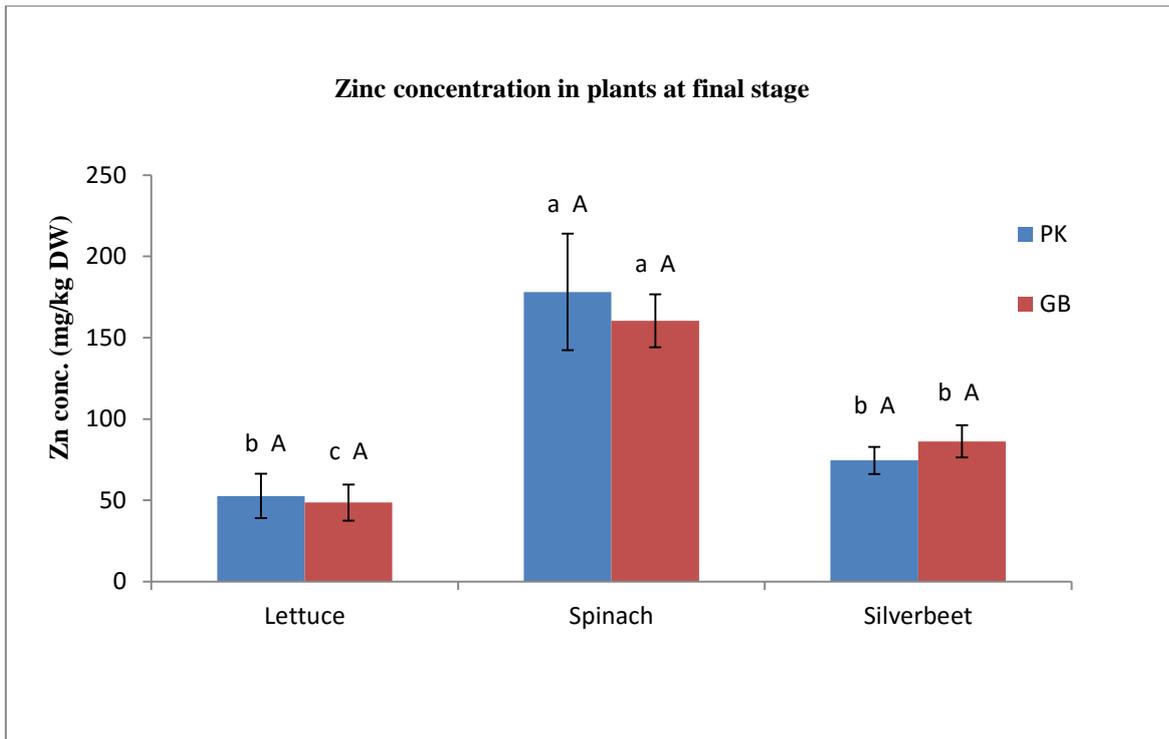
The Cd concentration in the three vegetables at final harvest was recalculated as a fresh weight concentration using the recorded water content of the harvested plants. The Cd concentration on a fresh weight basis is illustrated in Figure 17. The differences between the three leafy vegetables are significant for the Pukekohe soil (spinach  $0.104 \pm 0.02$  mg/kg FW, silverbeet  $0.048 \pm 0.013$  mg/kg FW, lettuce  $0.02 \pm 0.00$  mg/kg FW). Differences between the three species were again significant for the Gisborne soil (spinach  $0.266 \pm 0.06$  mg/kg FW, lettuce  $0.038 \pm 0.008$  mg/kg FW, silverbeet  $0.126 \pm 0.04$  mg/kg FW) with spinach reporting the highest Cd concentration.



**Figure 17:** Cadmium concentration (mg/kg FW) in plants at final stage. (i) Capital letters indicate differences in cadmium concentration between the two plants species grown on the same soil, and (ii) simple letters indicate differences in cadmium concentration for the same plant grown on different soils. Means with the same letter are not significantly different ( $p=0.05$ ). PK is the Pukekohe soil; GB is the Gisborne soil.

#### 4.5.4. Plant Zinc concentration in Pukekohe and Gisborne soil

The mean Zn concentration (mg/kg DW) in the three plant species at the final stage is shown in Figure 18. The Zn concentration in the vegetables grown on the Pukekohe soil followed this order spinach ( $178.1 \pm 35.8$  mg Zn/kg DW) > silverbeet ( $74.5 \pm 8.39$  mg Zn/kg DW) > lettuce ( $52.66 \pm 13.65$  mg Zn/kg DW) while the Zn concentration in vegetables grown on the Gisborne soil also followed the similar order spinach ( $160.44 \pm 16.34$  mg Zn/kg DW) > silverbeet ( $86.19 \pm 9.89$  mg Zn/kg DW) > lettuce ( $48.58 \pm 11.14$  mg Zn/kg DW). There were significant difference ( $P < 0.05$ ) between the three plant species grown on Pukekohe and Gisborne soil with spinach showing the highest Zn accumulation in both soils. There was no significant difference in Zn concentration for the same plant species between the two different soils (Pukekohe and Gisborne).



**Figure 18:** Zinc concentration (mg/kg DW) in plants at final stage. (i) Lower case letters indicate differences in zinc concentration between the three plants species grown on the same soil, and (ii) Upper case letters indicate differences in zinc concentration for the same plant grown on different soils. Means with the same letter are not significantly different ( $p > 0.05$ ). PK is the Pukekohe soil; GB is the Gisborne soil.

**Table 22:** Mean cadmium and zinc concentration in leafy vegetables in two New Zealand horticultural soils (at different stages)

Site location	Plant	1 <sup>st</sup> stage	Final stage	Final stage	Final stage
		Cd (mg/kg dry weight)		Cd (mg/kg FW)	Zn (mg/kg DW)
<i>Pukekohe</i>	Lettuce	NA	0.16 ± 0.02 <sup>c</sup>	0.02 ± 0.00 <sup>c</sup>	52.66 ± 13.65 <sup>b</sup>
	Spinach	1.03 ± 0.15 <sup>a</sup>	1.11 ± 0.1 <sup>a</sup>	0.1 ± 0.02 <sup>a</sup>	178.1 ± 35.8 <sup>a</sup>
	Silverbeet	0.56 ± 0.11 <sup>b</sup>	0.41 ± 0.07 <sup>b</sup>	0.05 ± 0.01 <sup>b</sup>	74.5 ± 8.39 <sup>b</sup>
<i>Gisborne</i>	Lettuce	NA	0.48 ± 0.06 <sup>b</sup>	0.04 ± 0.01 <sup>c</sup>	48.58 ± 11.14 <sup>c</sup>
	Spinach	1.61 ± 0.31 <sup>a</sup>	2.13 ± 0.50 <sup>a</sup>	0.27 ± 0.06 <sup>a</sup>	160.44 ± 16.34 <sup>a</sup>
	Silverbeet	1.21 ± 0.20 <sup>a</sup>	0.93 ± 0.26 <sup>b</sup>	0.12 ± 0.04 <sup>b</sup>	86 ± 9.89 <sup>b</sup>
<b>CODEX (2010)</b>				<b>0.2</b>	
<b>FSANZ (2011)</b>				<b>0.1</b>	
<b>Tolerable in agronomic crops (Kabata-Pendias &amp; Pendias, 2001)</b>		<b>0.05 – 0.5</b>			<b>50 - 100</b>

*Source:* Authors laboratory result

NA = Not analysed, DW = Dry weight, FW = Fresh weight.

**FSANZ** = Food Standard Australia New Zealand

#### **4.6. Heavy metal concentration in hemp and ryegrass (pasture) in impacted agricultural soil**

##### **4.6.1. Heavy metal concentration in hemp and ryegrass in 50:50mix of drilling waste/control soil**

The metal concentration in ryegrass and hemp for soil treatments is summarised in Table 23. The Zn and Cu concentration in ryegrass and hemp exceeded typical concentration for New Zealand pasture (Edmeades, 2013) and maximum tolerable limits in agronomic crops (Kabata-Pendias & Pendias, 2001) for all treatments, whereas the concentration for Cd and Ni was within normal range.

##### **4.6.2. Heavy metal concentration in hemp and ryegrass in 100% drilling waste**

The Zn and Cu concentration in hemp and ryegrass in 100% drilling waste was above both the typical concentration for New Zealand pasture (Edmeades, 2013) and allowable limits (Kabata-Pendias & Pendias, 2001) for agronomic crops (Table 23). However, the Zn and Cu concentration in hemp would pose no threat to animal welfare because it is a non-food product (no exposure pathway). The Cd concentration in hemp was also within typical New Zealand value for pasture but for ryegrass the concentration was above the New Zealand normal value.

##### **4.6.3. Heavy metal concentration in hemp and ryegrass in landfarm-impacted soil**

There was no significant difference ( $P > 0.05$ ) between the Cd concentration in hemp ( $0.1 \pm 0.0$  mg/kg) and ryegrass ( $0.1 \pm 0.0$  mg/kg) grown on landfarm-impacted soil (Table 23). Hemp showed a Ni concentration below detection limit while ryegrass accumulated Ni to a concentration of  $0.8 \pm 1.4$  mg/kg. There was no significant difference ( $P > 0.05$ ) between the Zn ( $69.0 \pm 14.9$  mg/kg;  $60.0 \pm 2.0$  mg/kg) and Cu ( $13.3 \pm 1.4$  mg/kg;  $9.6 \pm 2.3$  mg/kg) concentration in hemp and ryegrass on the landfarm-impacted soil respectively.

The Cd concentration in hemp and ryegrass grown on the landfarm-impacted soil was within typical New Zealand values for pasture (Edmeades, 2013). The Zn concentration in hemp and ryegrass exceeded New Zealand typical value for pasture. The Cu concentration in hemp exceeded the typical New Zealand value while the concentration in ryegrass was within the normal range. The Ni concentration in hemp was within typical New Zealand values for pasture while the concentration in ryegrass exceeded the typical value for New Zealand grown pasture. All the metals were within tolerable limits (Kabata-Pendias & Pendias, 2001) in agronomic crops (Table 23).

#### **4.6.4. Heavy metal concentration in hemp and ryegrass in control soil**

There was no significant difference ( $P > 0.05$ ) between the Cd concentration in hemp ( $0.1 \pm 0.0$  mg/kg) and ryegrass ( $0.1 \pm 0.0$  mg/kg) grown on the control soil. The Ni concentration in hemp was below the detection limit and  $3.2 \pm 1.5$  mg/kg for ryegrass. There was no significant difference ( $P > 0.05$ ) between the Zn ( $53.8 \pm 26.7$  mg/kg;  $57.1 \pm 16.0$  mg/kg) and Cu ( $11.7 \pm 4.0$  mg/kg;  $9.7 \pm 2.5$  mg/kg) concentration in hemp and ryegrass from the control soil respectively (Table 23).

The Zn concentration in hemp and ryegrass exceeded the typical value for New Zealand grown pasture. The Ni concentration in hemp was within the range of typical New Zealand values for pasture while the concentration in ryegrass exceeded the typical values for New Zealand grown pasture. The Cd concentration in hemp and ryegrass was within the typical New Zealand values for grown pasture. The Cu concentration in hemp exceeded the typical New Zealand value but was within for ryegrass (Edmeades, 2013). All metals analysed were within tolerable limits in agronomic crops (Kabata-Pendias & Pendias, 2001).

**Table 23:** Heavy metal concentration in Hemp and Ryegrass plants grown on all treatments applied

Treatment	Heavy metal concentrations in plant samples							
	Cd (mg/kg)		Zn (mg/kg)		Cu (mg/kg)		Ni (mg/kg)	
	Hemp	Ryegrass	Hemp	Ryegrass	Hemp	Ryegrass	Hemp	Ryegrass
50:50mix of drilling waste/control soil	0.1*	0.1*	201.5*	128.8*	23.1*	12.1*	BDL	BDL
100% drilling waste	0.1*	0.3*	144.7*	163.8*	37.6*	25.9*	BDL	BDL
Landfarm-impacted soil	0.1 ±0.0 <sup>A</sup>	0.1 ±0.0 <sup>A</sup>	69.0 ±14.9 <sup>A</sup>	60.0 ±2.0 <sup>A</sup>	13.3 ±1.4 <sup>A</sup>	9.6 ±2.3 <sup>A</sup>	BDL	0.8 ±1.4
Control soil	0.1 ±0.0 <sup>A</sup>	0.1 ±0.0 <sup>A</sup>	53.8 ±26.7 <sup>A</sup>	57.1 ±16.0 <sup>A</sup>	11.7 ±4.0 <sup>A</sup>	9.7 ±2.5 <sup>A</sup>	BDL	3.2 ±1.5
Typical concentration in pasture grown on New Zealand soil (Edmeades, 2013)	0.03 – 0.29		10 – 20		5 – 10		0.10 – 0.20	
Tolerable in agronomic crops (Kabata-Pendias & Pendias, 2001)	0.05 – 0.5		50 - 100		5 - 20		1 - 10	

*Source: Authors laboratory results*

*Data marked with (\*) indicates absence of replicate pots for the particular treatment,*

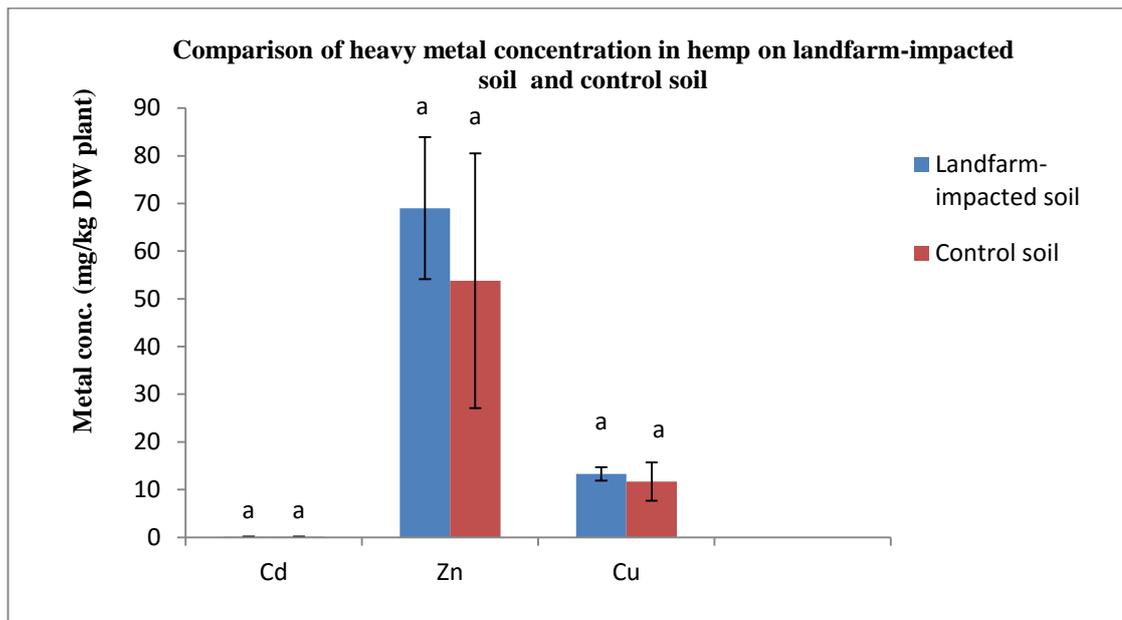
*BDL – Below detection limit (0.1 mg/kg).*

*Means of samples with same letters are not significantly different (P = 0.05) between plants for each metals*

*ng = not given*

#### 4.6.5. Comparison of heavy metal concentration in hemp in landfarm-impacted soil and control soil

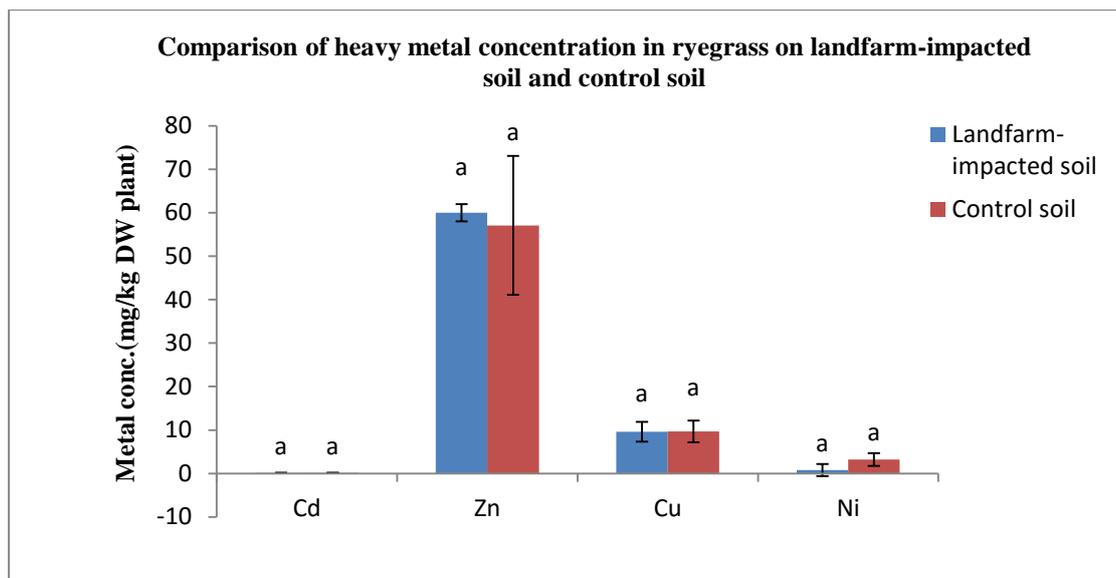
The Cd, Zn, Cu and Ni concentration in hemp on landfarm-impacted soil and control soil showed a similar pattern for nominal differences between the soils (Figure 19) but no statistically significant ( $P > 0.05$ ) difference.



**Figure 19:** Comparison of heavy metal concentration in hemp in landfarm-impacted soil and control soil. Lower case letters shows differences (comparisons) between each metal concentration in hemp in two treatments (landfarm-impacted soil and control soil). Same Letters indicates no significant difference ( $P > 0.05$ ).

#### 4.6.6. Comparison of heavy metal concentration in ryegrass on landfarm-impacted soil and control soil

The heavy metal (Cd, Zn, Cu, and Ni) concentration in ryegrass showed no difference between the landfarm-impacted soil and the control soil ( $P > 0.05$ ). Figure 20 shows no difference in the metal concentration in ryegrass as a function of landfarm waste addition to soil.



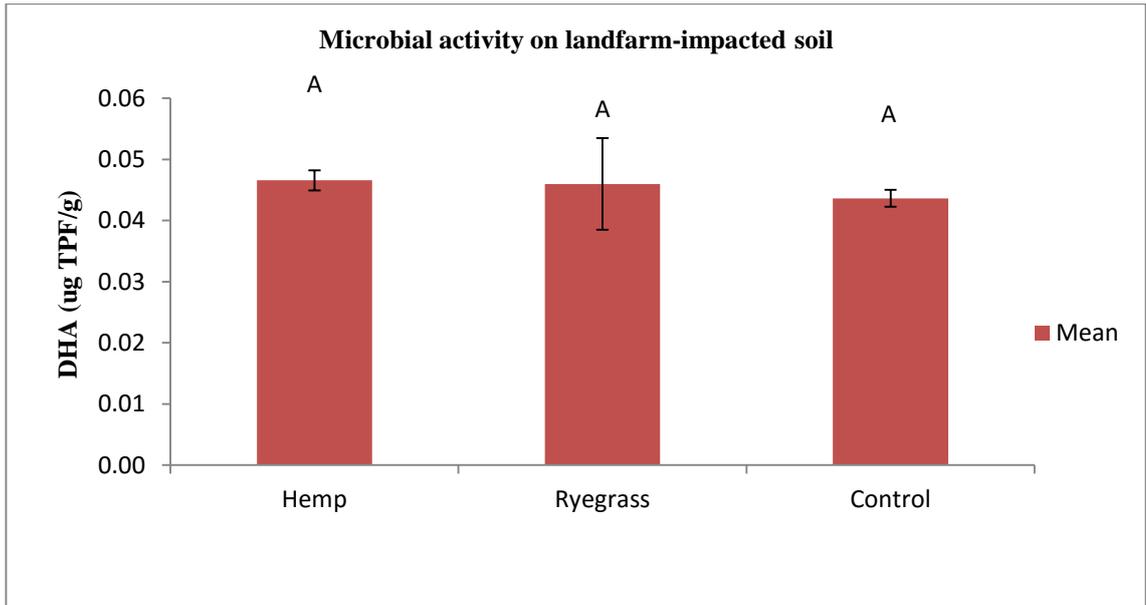
**Figure 20:** Comparison of heavy metal concentration in ryegrass in landfarm-impacted soil and control soil. Lower case letters shows differences (comparisons) between each metal concentration in ryegrass in two treatments (landfarm-impacted soil and control soil). Same Letters indicates no significant difference ( $P > 0.05$ ).

#### 4.7. Microbial activity in impacted agricultural soil

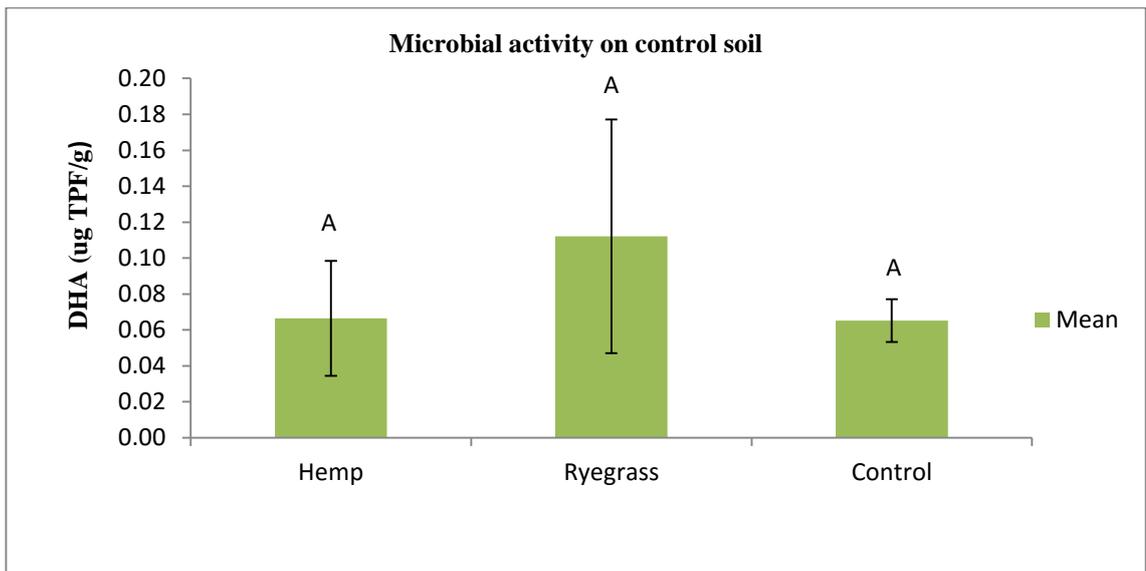
Comparison of the microbial activity in the landfarm-impacted soil and control soil planted with hemp and ryegrass showed no significant difference for the planted pots ( $P > 0.05$ ) when compared to the corresponding control soil without plants (Table 24; Figure 21 and 22).

**Table 24:** Microbial activity (DHA) in impacted agricultural soil

Samples	Dehydrogenase activity (ug TPF /g)			
	50:50 mix of Drilling waste and control	100% Drilling waste	Landfarm impacted soil	Control soil
Hemp	0.06	0.08	0.05 ± 0.00 <sup>A</sup>	0.07 ± 0.03 <sup>A</sup>
Ryegrass	0.08	0.06	0.05 ± 0.01 <sup>A</sup>	0.11 ± 0.07 <sup>A</sup>
Control (without plant)	0.05	0.06	0.04 ± 0.00 <sup>A</sup>	0.07 ± 0.01 <sup>A</sup>



**Figure 21:** Dehydrogenase activity (ug/g) in landfarm-impacted soil. Mean with same letter are not significantly different ( $P > 0.05$ ). This implies that no changes in microbial activities among hemp, ryegrass and control (without plant) pots for landfarm soil.

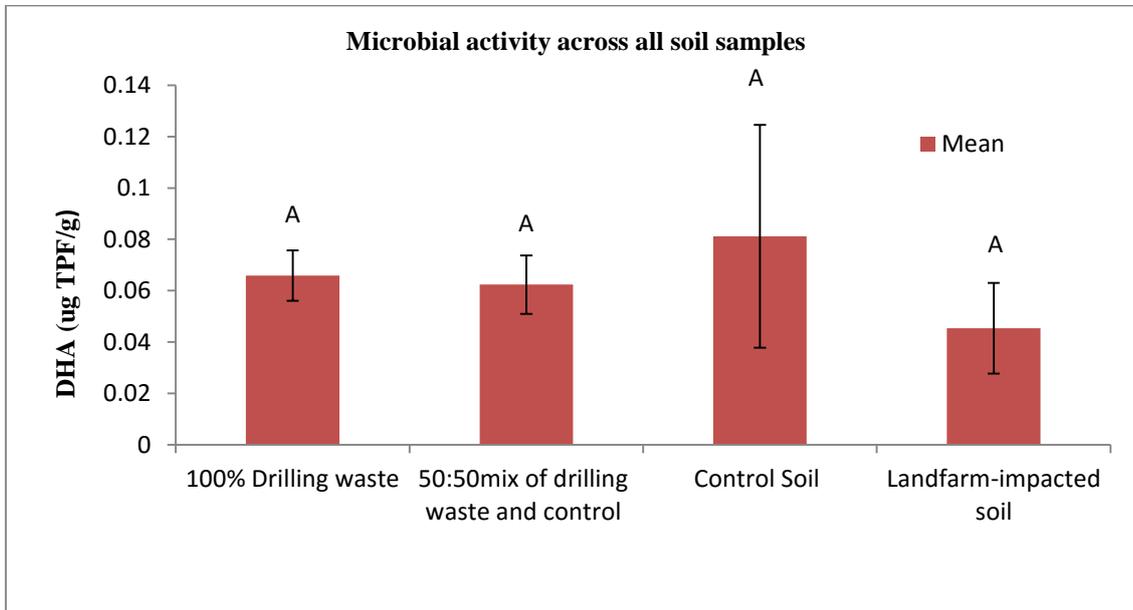


**Figure 22:** Dehydrogenase activity (ug/g) in control soil. Mean with similar letters are not significantly different ( $P > 0.05$ ). This suggests no change to microbial activity in control soil by hemp, ryegrass and control (no plant).

#### 4.7.1. Comparison of microbial activity across all soil samples

Figure 23 shows a comparison of microbial activity across all impacted agricultural soils. There was no significant difference ( $P > 0.05$ ) in microbial activity between all soil

samples. This implied that microbial activity in land impacted by drilling waste is at the same level with the control soil.



**Figure 23:** Comparison of dehydrogenase activity (ug/g) in all soil samples. Mean with similar letters are not significantly different ( $P > 0.05$ ). This suggests no change to microbial activity in control soil by hemp, ryegrass and control (no plant).

## **Chapter 5 : Discussion**

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### **5.1. Introduction**

In this Chapter the results presented in Chapter four will be interpreted and discussed in the context of the specific objectives of this study stated in chapter one. Similarities or differences between my findings and past literature is discussed. Comparison of heavy metal accumulation in the different land use types studied and consideration of risk-based guidelines (biosolids guidelines) will enable a useful analysis of the risks associated with the heavy metal inputs to different New Zealand agricultural soils. As described in the previous chapter, horticultural soil describes two soils sourced from commercial farms in Pukekohe and Gisborne that contrast in soil properties. Impacted soil describes different soil treatments: landfarm-impacted soils, 50:50mix of drilling waste/control soil, 100% drilling waste and a control soil. It is important to note that drilling waste is not an actual soil (100% industrial waste) and represents a different environmental scenario to the landfarm-impacted soil described in chapter three.

The heavy metal concentration in plants and soils relative to risk-based guidelines will be discussed in the context of soil reactions influencing heavy metal accumulation in soil. Other soil factors influencing heavy metal bioavailability will be discussed. Finally, the phytoremediation potentials of hemp and the influence of this plant on impacted soil in the context of the landfarming are discussed.

### **5.2. Heavy metal concentration in plants and agricultural soils relative to risk-based guidelines**

#### **5.2.1. Horticultural**

The results of this study suggest that total cadmium in horticultural soils (Pukekohe and Gisborne) is below soil quality guidelines for the safe application of biosolids to land. The soil quality guideline for safe application of biosolids ensures protection of food

safety, trade, human and animal welfare (NZWWA, 2003). This implies that the history of fertiliser use on this land does not present threats to animals from soil ingestion. This also suggests that the soil Cd concentration will not pose a threat to food safety standard, animal and human welfare. However, the only way to accurately assess food standard risks is to analyse the plant metal concentrations in those soils. The Cd concentration in the two horticultural soils were at tier 0 of the TFMS which defines a need for a five-yearly screening soil test for cadmium status to monitor for any future Cd elevation in those soils.

Food quality guideline concentrations for cadmium in vegetables (fresh weight (FW)) have been defined to be 0.2 mg/kg FW by CODEX (2010) and 0.1 mg/kg FW by FSANZ. An exceedance of these guidelines values does not define a direct risk to human health, but could impact on the accessibility of such products to export markets. The risk of Cd to human health is assessed by evaluating the daily cadmium intake per different age groups (Cavanagh, 2014). This however, is not the focus of this study. In addition, the tolerable limit of Cd and Zn in agronomic crops (Kabata-Pendias & Pendias, 2001) has been used to evaluate the risk of these metal concentrations. The concentration of Cd in lettuce and silverbeet grown on both soils was below these guideline values and therefore Cd has no impact on the value chain for these products. The situation for spinach, however, is more complicated. Spinach grown on the Pukekohe soil was at the FSANZ (2011) authority guideline for Cd, but below the CODEX (2010) value. Spinach grown on the Gisborne soil (both baby spinach and final harvest or full leaf spinach) exceeded both the FSANZ (2011) and CODEX (2010) guideline. The Cd concentration in spinach harvested from the Gisborne soil is therefore a potential threat to export markets. Of the three vegetable species tested in this trial, spinach has the greatest potential to accumulate Cd from soil. The Cd concentration

(FW) in lettuce grown on Gisborne soil was below CODEX (2010) – 0.2 mg/kg FW and FSANZ (2011) trigger value, below and above CODEX (2010) and FSANZ (2011) trigger value for silverbeet respectively. All the leafy vegetables analysed in this study also exceeded the tolerable Cd limits in agronomic crops in the two soils at all stages with the exception of silverbeet in Pukekohe soil at final stage. The high Cd concentration above risk guidelines undermines the efficiency of the biosolids guidelines (NZWWA, 2003). Based on this, a reviewed biosolids guideline that will consider cadmium pathways in different plant species is necessary for the protection of relevant endpoints in New Zealand.

#### **5.2.2. Impacted soil**

The Cd, Zn, Ni and Cu concentration in all landfarm-impacted soil treatments was below soil quality guideline for safe application of biosolids (NZWWA, 2003). This finding is supported by Cavanagh (2015) and Edmeades (2013) that reported a zero threat of heavy metals from landfarm-impacted soil. However, comparison of heavy metal concentrations in all impacted soil treatments with typical values for New Zealand farmed soil (Edmeades, 2013) suggests that Zn and Cu concentrations exceeded typical New Zealand concentration for agricultural soils. This is however, not an issue as Cu and Zn are essential nutrients that supports plant growth at concentration below toxic levels (and even the control soil showed higher than normal). The results of this study suggest that the application of drilling waste to Taranaki soil has not increased soil metal concentrations above risk-based guideline levels. The low concentration of heavy metal in all soil samples may be attributed to low metal concentration in the drilling waste. Application of drilling waste to agricultural soils potentially offers an opportunity for Cu/Zn deficiency amendment.

The Cd and Nickel concentration in ryegrass in all impacted soil treatments was within tolerable levels for agronomic crops. In general, it could be said that land application of drilling waste to soil has not elevated the Zn and Cu concentration in ryegrass and pasture. However, the Cu concentration in ryegrass in 100% drilling waste exceeded the tolerable limits for agronomic crops but was within tolerable limits for all other impacted soil treatments. The Zn concentration exceeded the tolerable limit for the 50:50 mix of drilling waste/control soil and for the 100% drilling waste but was within the limit for landfarm-impacted soil and the control soil. The visual observation (chapter 3) of plants in 100% drilling waste and 50:50 mix of drilling waste/control shows that this medium is unsuitable for plant growth. This is unlikely to occur on landfarm area. However, application of waste would be at a rate where the soil: waste ratio is much lower than 50:50.

For the landfarm-impacted soil experiments, soil heavy metal concentrations below risk-based guidelines are in agreement with plant metal concentrations that are also below 'safe' values. This supports the acceptance of the risk-based guidelines used in this work as an efficient document for managing contaminants in agricultural soils impacted by landfarming activities.

### **5.3. Influence of soil reaction on heavy metal concentration in plants**

#### **5.3.1. Cd/Zn effects**

Zn is an essential nutrient for plant growth and development and has a suggested role in Cd regulation in plants (Sarwar et al., 2010). Hart et al. (2005) proposed that Zn addition to soil reduces Cd tissue concentration by inhibiting Cd uptake in roots. Similar studies have shown that increasing or decreasing Cd and Zn concentration in soil may have either synergistic or antagonistic effect on plant growth (Tamboli & Rai, 2015;

Tkalec et al., 2014; Nan et al., 2002). Tkalec et al. (2014) reported high Zn uptake by plant tissues when exposed to high Zn (50  $\mu\text{M}$ ) and low Cd (10  $\mu\text{M}$ ) concentration respectively. Tamboli & Rai (2015) also affirmed that low soil Cd concentration introduces Zn antagonistic effects while high Cd adversely affects plant growth showing a synergistic effect of the two metals. This study reported no antagonistic effects of Cd and Zn due to absence of correlation between Zn and Cd. However, the difference in Cd and Zn concentrations in Pukekohe and Gisborne soil is more likely a factor of the high versus low allophane contents of the two soils impacting bioavailability.

### **5.3.2. Oxalate extractable Al and Fe**

Quantification of concentration, distribution and form of Al and Fe oxides in contaminated soil is relevant for the assessment of colloidal-influenced movement of contaminants and uptake by plants (Shaw, 2001). Al and Fe oxides are introduced into the soil through the primary weathering of minerals (Shaw, 2001). Soil pH and Al and Fe oxides are the most significant soil factor influencing metal availability and fractionation in contaminated soils (Su, 2010). Metals accumulate more in high clay or Al and Fe oxalate containing soils due to the adsorption of metals to the clay surfaces (Mann et al., 2002). Su (2010) reported low metal availability in a soil with high pH level and high Al and Fe oxide greater than 20 g/kg. Similarly, Al-oud et al. (2014) reported decreasing Cd bioavailability with increasing amount of Fe oxides. The results of the current study affirm the findings of Mann et al. (2002); Su (2010) and Al-oud et al (2014) as higher oxalate extractable Al and Fe was found in the Pukekohe soil than the Gisborne soil. Relatively higher pH and higher extractable Al and Fe oxalate concentration in the Pukekohe soil provides an explanation to the lower extractable soil Cd (bioavailable Cd) observed for the soil than in Gisborne soil despite a higher total

Cd concentration. This suggests that these soil factors play a significant role to Cd bioavailability to plants and concentration in soil.

## **5.4. Soil properties influencing heavy metal concentration in soil and plant in New Zealand**

### **5.4.1. Soil pH and Organic matter**

#### **5.4.1.1. Horticultural soils**

Soil pH plays a vital role in soil chemical and physiological processes and plant nutrient and metal bioavailability (Hill laboratory, 2016a). The total extractable (bioavailable) cadmium concentration was significantly greater in the Gisborne soil than in Pukekohe soil. In addition, there was also a significant difference in the Cd concentration between each plant species planted on the different soil (Pukekohe and Gisborne) with a higher Cd concentration observed in plants (lettuce, spinach and silverbeet) grown on Gisborne soil than Pukekohe soil. However, the observed differences in plant and soil cadmium concentration between the two horticultural soils may be attributed to the differences in their soil chemistry. Low soil pH level influences metal bioavailability leading to high chances of plant metal uptake thereby reducing its soil concentration (Kirkham, 2006; Mann et al., 2002). The pH level in Pukekohe soil was greater than in Gisborne soil. This implies that soil pH level promotes Cd bioavailability and accumulation in plants.

The presence of soil organic matter decreases heavy metal bioavailability thereby leading to adsorption of heavy metal to organic matter hence increased soil accumulation (Mann et al., 2002). Organic carbon and nitrogen contents of the two horticultural soils were observed to be low as well as their C/N ratio. The difference in pH level and oxalate extractable Al and Fe of the two soils therefore provides a better explanation for the observed higher Cd in leafy vegetables on Gisborne soil

#### **5.4.1.2. Impacted soil**

The elevated pH level in the landfarm-impacted soil and 100% drilling waste suggests that land application of drilling waste raises soil pH from what it was in the control soil. Differences in soil pH among the control soil, landfarm-impacted soil and 100% drilling waste were not related to variable Cd concentration. The lower Zn concentration in the 100% drilling waste may be attributed to initial low metal concentration in the waste. Elevated Zn, Cu, Cd (ryegrass in 100% drilling waste) and Ni (in ryegrass in landfarm-impacted soil and control) concentrations in hemp and ryegrass above their corresponding soil concentrations suggests bioavailability of these metals in the soil. The bioavailability of metals was primarily influenced by pH level as higher Zn, Cu and Ni accumulation in plants was observed in soil with lower pH levels.

#### **5.4.2. CEC, Extractable cations & Base Saturation**

Extractable cations (K, Ca, Mg and Na) are an essential group of nutrients vital for plant growth and their availability to plants is determined by soil CEC (Hill laboratory, 2016a). CEC measures the soil's capacity to hold extractable cations; this implies that low CEC will result in a low concentration of essential extractable soil cations (Hill laboratory, 2016a). CEC is highly correlated with soil organic matter content and low CEC suggests low soil organic matter (Hill laboratory, 2016b). Base saturation is the proportion of cation exchange sites occupied by extractable cations (Hill laboratory, 2016a). Cation exchange capacity is more often used in soil quality interpretation than base saturation as it provides a clear indication of available cation exchange sites (Hill Laboratory, 2016a).

#### **5.4.2.1. Horticultural soils**

Pukekohe soil has a lower cation exchange capacity and concentration of extractable cations (except K) than Gisborne soil. However the two soils showed a normal CEC

range for plant growth or soils in New Zealand. In an ideal agricultural soil, the magnesium level should be twice that of potassium to avoid suppression of magnesium uptake by potassium, while sodium is only of secondary value to crops (Hill laboratory, 2016a). Based on the Mg and K level, the Gisborne soil can be said to be more ideal for plant growth than Pukekohe soil and this may be as a result of the difference in their pH level. Since soil pH is a major factor influencing soil processes, cation exchange capacity can be said to be influenced by soil pH level. In other words the lower CEC in the Pukekohe soil than in the Gisborne soil can be said to a factor influencing Cd accumulation in soil more strongly than plant accumulation. However, the studied horticultural soils are both good soils (because of CEC within medium range) and so imply that the balance of cations is not an issue.

#### **5.4.2.2. Impacted soil**

100% drilling waste, landfarm-impacted soil and the control soil have a very low CEC. The extractable cations for the control soil were low indicating that the soil chemical properties may suppress plant growth. Low CEC in all soil treatments did not affect the Cd concentration in soil. Our findings shows increasing plant accumulation of Cu (hemp and ryegrass), Cd (only in ryegrass), Zn (hemp and ryegrass) and Ni (in ryegrass) in all treatment with increasing CEC against the corresponding soil with lower Cd concentration. Based on this result, it can be said that low CEC of a soil increases metal bioavailability, chance of uptake by plants and potential high loss of metals through leaching. Landfarm-impacted soil showed higher base saturation than the control soil. This implies a presence of higher cation exchange sites in landfarm-impacted soil than in control soil.

### **5.4.3. Soil Olsen P level**

#### **5.4.3.1. Horticultural soil**

The Olsen P values for both soils were high relative to the background concentration of Olsen P in New Zealand soils. The Pukekohe soil had a higher Olsen P concentration (81.33 mg/L) than the Gisborne soil (49.67 mg/L) indicating high rate of P fertiliser application more than longer history of P fertilisation. As Cd concentration in soil is generally a function of history of Phosphate fertilisation, soils with a high Olsen P concentration may potentially have an elevated total Cd concentration (Mann et al., 2002). This is the case for this study where high Cd concentration was observed in Pukekohe soil than in Gisborne soil.

#### **5.4.3.2. Impacted soil**

Low Olsen P level was observed in 100% drilling waste with the highest value observed in landfarm-impacted soil and a normal value in control soil. However, the increased Olsen P level is an indication that landfarm waste contains more P fertiliser than the control soil prior to sample collection. The difference between 100% drilling waste and landfarm-impacted soil was described in the previous chapter. Drilling waste is a hypothetical treatment while landfarm-impacted soil represents an agricultural soil that has been impacted by drilling waste. Lower Zn and higher Cu concentration was observed in 100% drilling waste with low Olsen P level. The finding of this research is that 100% drilling waste is not suitable for pasture or hemp production.

### **5.5. Potential of hemp for phytoremediation**

Hemp's ability to accumulate and produce high biomass in contaminated soil was assessed and compared with ryegrass. Hemp is often proposed as a phytoremediation plant species due to superior biomass potential and metal uptake. The potential value of hemp as a phytoremediation agent for landfarm-impacted soil is a parameter that can

inform decision making on alternative plants with economic value to be grown on landfarm-impacted land. The phytoremediation potential of hemp was assessed through observation of hemp biomass and heavy metal accumulation in impacted soil. Comparison of average hemp biomass in soil impacted by drilling waste and control soil (Table 25) showed no significant difference ( $P>0.05$ ). Hemp biomass and metal uptake in 50:50 mix of drilling waste/control and a 100% drilling waste also showed low nominal values. There was no significant difference ( $P>0.05$ ) between Cd, Zn and Cu uptake by hemp in soil impacted by drilling waste and control soil (Table 25).

**Table 25:** Heavy metal uptake by hemp and hemp biomass in impacted and control soil samples

Soil/treatment	Biomass (g)	Biomass (g/pot)	Heavy metal uptake by hemp ( $\mu\text{g}/\text{pot}$ )		
			Cd	Zn	Cu
Landfarm	$3.33 \pm 1.26^A$	$0.09 \pm 0.03^A$	$0.01 \pm 0.0^A$	$6.01 \pm 1.88^A$	$1.2 \pm 0.44^A$
Control soil	$2.65 \pm 0.69^A$	$0.07 \pm 0.02^A$	$0.01 \pm 0.0^A$	$3.69 \pm 1.50^A$	$0.89 \pm 0.52^A$
50:50mix of Drilling waste and control soil	0.0757*	0.002	0.00	0.42	0.05
100% Drilling waste	0.0864*	0.002	0.00	0.34	0.09

\* = Samples without replicate pot, A = Samples with same letters shows no significant difference ( $P > 0.05$ ) across treatments.

Although hemp is not a hyperaccumulator, high biomass quality and heavy metal accumulation without plant damage was observed in this study. However, the lack of defined soil contamination observed for all soil treatments in this study means that remediation is, in fact, not necessary.

It is clear from this study that pasture growth on landfarm-impacted soil presents no threat to the New Zealand agriculture. The public perception on plant and soil heavy metal accumulation in landfarm-degraded land is not supported by this study. Our study also proves that the halt in milk collection from landfarm-impacted soil by dairy industries due to perceived heavy metal accumulation is without scientific backing. The presence of contaminant exposure pathways in a degraded environment is a clear indication of perceived risk. In case of continuing public and dairy industry concern on potential heavy metal risk in landfarm-impacted soil, hemp (a non-food crop with no metal exposure pathway to animals and humans) cultivation provides an alternative choice to ryegrass (with direct and indirect exposure pathway to animals and human respectively). Based on that, seasonal cultivation of hemp could be carried as an alternative land-use for impacted soils. Hemp could also be planted and harvested prior to pasture growth to reduce chances of metal accumulation by pasture. Soil microbial activity is very essential to nutrient cycling, mineralisation and organic matter and plant nutrient transformation (essential for phytoremediation) (Dick & Tabatabai, 1993). The effect of impacted soil and different plants (ryegrass and hemp) on microbial activity is discussed in the next section.

### **5.5.1. Influence of land application of drilling waste to soil microbial activity**

The result of this study suggests no alteration to soil microbial activities as a result of drilling waste application to land. The result also suggests that hemp and ryegrass cultivation did not cause any change to soil microbial activity. This is in contrast to Marin et al. (2005) and Pajares et al. (2011) who reported improvement in microbial activity with application of drilling waste and organic manure (animal dung, crop residue etc). However, the experiments in this thesis did not include organic manure which would provide a readily available C source for microbial activity so increased activity is hardly surprising. Our findings may also be attributed to microorganism adaptation and exhaustion with time (Cavanagh et al., 2014). This idea implies that microbial activity (dehydrogenase activity) on landfarm-impacted soil decreases with decreasing hydrocarbon content and time as a result of contaminant degradation by soil microorganism (Marin et al., 2005).

## **Chapter 6 : Conclusion and Recommendations**

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### **6.1. Context**

This study evaluated heavy metal concentration in two different agricultural soils (horticultural soil and soil impacted by drilling waste) in a glasshouse located at Massey University's Plant Growth Unit. The aim of this work was to assess heavy metal accumulation in New Zealand agricultural soil impacted by fertilisers and drilling waste and factors influencing their accumulation in economically important crops. This study also sought to identify potential risk to food safety, trade, animal welfare and human welfare associated with New Zealand impacted agricultural soils. A hypothesis that landfarm-impacted soil is suitable for pasture cultivation was also verified in this study. Key findings of this research are summarised in this final chapter.

### **6.2. Conclusion and Future research**

An elevated soil and plant Cd concentration in New Zealand horticultural soils is associated with phosphate fertiliser. Landfarming on agricultural soils has the potential to increase the Cu and Zn concentration of soil. The application of drilling waste to agricultural land may not, however, be an environmental problem. The Zn/Cu deficiency issue is minor and no deficiencies demonstrated.

Soil pH is a dominant factor influencing soil heavy metal (Zn, Cd, Cu and Ni) bioavailability in horticultural and impacted soils. The distinction between the base saturation in landfarm-impacted soil and a control soil is an indication that heavy metals can easily be adsorbed and therefore less bioavailable in landfarm-impacted soil than in control soil. However, this was not supported by the experimental data as there was no difference in plant and soil heavy metal concentration of the two soils. Organic matter and clay minerals waste will strongly absorb heavy metals such as cadmium thereby

reducing its bioavailability and plant uptake. Assessment of organic matter and oxalate extractable Al and Fe in the horticultural soil allowed for an explanation of relative Cd uptake between the two soils. However, the presence of these components in the drilling waste was not tested and this is an area for further studies. The low microbial activity of the impacted soil could be an indication of low organic matter content. The results of this study suggest that soil organic matter improvement is a key opportunity to minimise cadmium uptake by plants.

The pedogenesis of the two horticultural soils is different. The Pukekohe soil is derived from volcanic ash, whereas the Gisborne soil is a Recent Soil from river sediment and has had variable input of volcanic ash. The allophane content of the Pukekohe soil, as quantified by the concentration of amorphous Fe and Al, was higher than that for the Gisborne soil supporting the greater influence of volcanic parent material in pedogenesis. Allophane has potential to adsorb Cd, and the recorded allophane content is in agreement with the relative ordering of Cd uptake by the tested plants on the two horticultural soils. These important soil properties (pH and allophane) offer an explanation for the higher concentration of bioavailable Cd in the Gisborne soil relative to the Pukekohe soil. This study highlights that the extractable Cd concentration is better correlated with plant Cd than the total Cd concentration in the soil. On the other hand, the pedogenesis of the impacted soil was not studied but soil pH level suggests the influence of soil acidity on the heavy concentration in ryegrass and hemp above their corresponding soil concentration.

Soil Olsen P level in the two horticultural soils suggests high rates of P fertilisers use on those soil while the elevated Olsen P level in the landfarm-impacted soil suggest the presence of P fertiliser in landfarm waste prior to soil sampling.

There is no evidence of heavy metals (Zn, Ni, Cu and Cd) concentration above soil limits for safe application of biosolids in either the horticultural or landfarm-impacted soils studied in this research. This suggests that animal wellbeing (via soil ingestion) and food safety will not be affected as a result of land application of drilling waste and a long history of P fertiliser use. However, the major concern is on the exposure pathways via plant uptake (vegetables, pasture and fibre).

The Cd status of the two horticultural soils and the landfarm-impacted soils are at tier 0 of the TFMS which implies that farmers will require five-yearly screening soil test to maintain this cadmium status. However, no fertiliser management protocol is necessary to prevent future Cd accumulation in soil. The results on heavy metal concentration in landfarm-impacted soil reported in this thesis provide more evidence to the public and New Zealand dairy industry that landfarming does not pose a risk to agricultural value chains.

Spinach and silverbeet have the potential to accumulate Cd to a concentration that exceeds guideline levels from soil with a total Cd concentration that would not be regarded as high enough to assess likely environmental (food safety, animal and human welfare) risk. Spinach, in particular, appears to be an efficient Cd accumulator plant, where soil geochemical conditions promote bioavailability. It can be concluded that horticultural soils with high rates of P fertiliser use may promote a significant Cd in spinach to the level that represents a threat to food safety and trade. This suggests a more extensive study of dietary intake of Cd containing spinach is needed which will assist in a comprehensive assessment of its potential threats to human welfare. Lettuce has less potential for Cd accumulation. The elevated heavy metal accumulation by leafy vegetables, ryegrass and hemp above soil background also calls for the re-evaluation of

biosolids guidelines or development of a specific guideline that will consider metal pathways in different plant species, cultivars or varieties.

Ryegrass (pasture) and hemp show limited risk of accumulating Cd, Zn, Cu and Ni above tolerable limits from landfarm soils. Elevated Cu and Zn concentrations in hemp in a 50:50mix of drilling waste /control soil and 100% drilling waste above the tolerable limit in this study is not a problem, as there is no practical scenario where agricultural production would be conducted on soil that contained such a high rate of drilling waste. The data recorded in this research has potential to be used to support better definition of drilling waste application rates required for landfarming suitability in New Zealand.

Microbial activity (dehydrogenase activity) was not affected by the application of drilling waste to land. Planting hemp and ryegrass did not affect different soil microbial activity. However, these findings are provisional. The age of the accessed landfarm-impacted soil should be better understood and changes in microbial activity over time assessed to better understand the implications of landfarming on soil microbiological activity.

There was no difference between heavy metal accumulation by hemp and ryegrass in landfarm-impacted soil and control soil and recorded levels of heavy metals were below all environmental quality guidelines. This implies that the landfarming soil does not meet the regulatory criteria for contaminated land, and therefore remediation is not necessary. However, public concern over the suitability of landfarming soil for agriculture remains. Hemp as a non-food product with limited metal exposure pathways to animals that could be planted at an early stage of landfarm then harvested and utilised for its fibre quality prior to pasture growth. Metal uptake and removal from soil with hemp (a function of its increased biomass relative to ryegrass) could further support an

economic analysis of growing hemp on landfarm-impacted soil. Hemp could be explored as an alternative land use option for land-farm impacted soil to limit negative public perception on landfarming suitability in New Zealand.

There is need for an extension of this study to accommodate other crops grown on New Zealand horticultural soils to support a comprehensive knowledge of cadmium behaviour. This will support the development of specific soil guideline values for cadmium management in New Zealand. This work should continue to investigate soil parameters that may be promoting Cd bioavailability and is necessary to better understand the potential risks that Cd in vegetable crops may have on the export earnings of this primary production sector. Better understanding of these risks will allow for the design of appropriate risk management plans.

With respect to landfarming, ongoing evaluation of the heavy metal component of New Zealand drilling waste is required to ascertain the level of reduction that is afforded by landfarming and consequent increase in element composition of soil. Quantifying the heavy metal balance in landfarm-impacted soil and allocating crop cycles to such land based on risks (real or perceived) will support the logic for land-based disposal of drilling waste and convince the public of the transparency of the system.

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## Appendix 1: Cadmium concentration of phosphate rocks

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### Cadmium and New Zealand Soils

Dominant source of cadmium on New Zealand agricultural top soil originated from overuse of phosphate fertilisers produced from varied phosphate rocks imported into New Zealand. Those phosphate rocks involve Superphosphate (SSP), triple superphosphates (TSP), diammonium phosphate (DAP) or partially acidulated phosphate rock (PAPR) manufactured through acidulation of phosphate rock. Table A1 below shows cadmium, fluorine and phosphorus concentration of reactive phosphate rocks. These contaminants (Cadmium and Fluorine) concentrations results from a long term use of phosphate fertilisers in New Zealand top soil (Clovertone Ltd, no date).

**Table A 1:** Cadmium concentration in different P fertiliser sources used in New Zealand (Clovertone Ltd, no date)

Phosphate Rocks	Cadmium (mg/kg)	Fluorine (%)	Phosphorus (%)
Kola	0.2		17.2
Chatham Rise	2	3.0	8.9
North Florida	3	4.0	13.3
Phalaborwa	3		17.2
Jordan	5	3.8	14.0
Egypt (Quasar)	8	4.0	12.7
Mexico	8	4.1	14.0
Makatea	10	3.2	13.0
Sechura	11	3.4	13.1
Arad	12	4.0	14.1
Khouribga	15		13.8
Syria	16		13.3
Algeria	18		12.5

<b>Gaffs</b>	38	4.1	13.4
<b>Morocco (Boucraa)</b>	38		15.7
<b>Youssoufia</b>	40		14.2
<b>North Carolina</b>	41	3.5	13.0
<b>Christmas Island</b>	43	2.2	15.3
<b>Togo</b>	60		15.9
<b>Taiba</b>	75		15.9
<b>Senegal</b>	87		
<b>Ocean Island</b>	99		
<b>Nauru</b>	100	3.0	15.6
<b>SSP</b>	5 - 30	1.08 – 1.84	9.0
<b>TSP</b>	70	1.3 – 2.4	21
<b>DAP</b>	7 – 75	1.2 – 3.0	20

## Appendix 2: Cadmium Management Strategy

Core areas of Cadmium Management Strategy is summarised below in table A2.

**Table A 2 :** Core areas of Cadmium Management Strategy in New Zealand

<b><i>Food monitoring</i></b>	This is the primary tool for managing the risk of food containing cadmium to human health and trade (MAF, 2011). The proposed food monitoring risk management framework that will be implemented by the Cadmium Management strategy has three levels: identify, Assess and manage. Full details of the three levels are documented in MAF (2011).
<b><i>Soil Monitoring</i></b>	This is a tool that evaluates the continuous cadmium status and its pattern of accumulation (over time) in New Zealand soil (MAF, 2011). Fertilizer industry, regional council, farmers and research organisations are charged with the responsibility of monitoring soils for cadmium status (MAF, 2011). Fertilizer industry through its self-management programme regularly test soils for cadmium, FertResearch coordinates soil monitoring while the regional council covers this area through their State of Environment (SoE) reporting (MAF, 2011).
<b><i>Fertiliser monitoring</i></b>	This is a vital part of managing cadmium accumulation in agricultural which entails monitoring of cadmium levels in phosphate fertilizers by Fertilizer Quality Council (MAF, 2011). It is a self-governed approach to regulating the maximum permissible cadmium concentrations (MPC) in phosphate fertilizers sold and used in New Zealand (Stafford et al., 2014). Maximum permissible concentration of cadmium in phosphate fertilizer has been progressively reduced to 280mg Cd/kg (Table 1) from what it was in the past (prior to 1995) and constant self-governed testing within Fertmark quality assurance scheme was behind this achievement (Stafford et al., 2014). Fertilizer monitoring is carried out through an association of fertilizer company laboratory reporting and Fertmark random assessment at dispatch locations all over New Zealand (MAF, 2011). It is the responsibility of fertilizer industry to apply Fertmark method in their

	<p>continuous test for cadmium levels in products and subsequently report to Fertilizer Quality Council in charge of auditing the produced reports (MAF, 2011). Audited reports are submitted to Cadmium Management Group annually to ensure continuous cadmium management (MAF, 2011).</p>
<p><b><i>Fertiliser management</i></b></p>	<p>An industry based programme developed under this strategy aims to maintain cadmium in soil at levels that poses minimal risk to soil health and its appropriateness for use as a medium for agricultural activities (MAF, 2011). The industry based programme is based on a tiered management system called Tiered Fertiliser Management System (TFMS), a system that connects phosphate fertilizer use and increasing soil cadmium levels with a specific management action (MAF, 2011).</p>

### Appendix 3: Trace elements in New Zealand soils

The background trace element concentration in a typical and representative New Zealand soil is shown here in table A3 (a, b, c) below.

**Table A 3:** Trace elements (mg/kg) in (a) Auckland soil, (b) Waikato soil and (c) Tasman Soil (Gaw et al., 2006)

#### (a) Auckland soil

Land use	As	Cd	Cu	Hg	Pb	Sn	Zn
Market garden	6	0.7	51	0.2	24	2	62
Orchard	15	0.4	224	0.1	76	2	62
Vineyards	7	0.4	107	0.2	62	2	77
Grazing	2	0.4	22	<1	18	<1	42
Background	5	0.12	13	0.13	16	0.9	39

#### (b) Waikato soil

Land use	As	Cd	Cu	Hg	Pb	Sn	Zn
Market garden	9	0.5	60	0.3	33	3	78
Orchard	18	1.1	344	0.4	77	5	119
Vineyards	10	0.3	71	0.1	35	2	89
Grazing	6	0.7	20	0.1	24	1	67
Background	6	0.1	18	0.2	29	1	46

#### (c) Tasman soil

Land use	As	Cd	Cu	Hg	Pb	Sn	Zn
Market garden	10	0.2	40	<0.1	13	<1	90
Orchard	30	0.5	58	0.2	149	3	70

<b>Tobacco (historical use)</b>	2	0.3	27	<0.1	10	<1	63
<b>Grazing</b>	3	0.4	19	<0.1	9	<1	47

## Appendix 4: Minimum levels of contaminants in food

Specific criteria to be considered in determining minimum levels of contaminants in food are as follows (CODEX, 2010):

**Table A 4:** Criteria to be considered in determining minimum levels of contaminants in food (CODEX, 2010)

Specific Criteria	Desired information
<i>Toxicological information</i>	<ul style="list-style-type: none"> <li>• Identification of toxic substance</li> <li>• Metabolism in humans and animals</li> <li>• Toxicokinetics and toxicodynamics involving information on likely carry-over of the contaminant from feed to edible animal tissues/products.</li> <li>• Facts on prolonged toxicity in animals and humans involving epidemiological data on humans and other important toxicity data</li> <li>• Conclusion and recommendation of toxicological experts, with references including facts on specially defenceless group of a population or animals</li> </ul>
<i>Analytical data</i>	Information on analytical procedure, samples and a statement of the representative sample of the contaminated products is very vital.
<i>Intake data</i>	Contamination concentration in a food or food group responsible for 50 to 80% or more of the total dietary intake of contaminants by consumers is required. Food consumption data for average and most exposed and susceptible consumer group is also relevant.
<i>Technological considerations</i>	Information on contaminant sources and the way the food is contaminated is also required.

## Appendix 5: Hierarchy of soil guideline documents used in TFMS trigger value formulation

Selection of the under listed documents was based on specific criteria addressing different endpoint of concern in New Zealand (MAF, 2011). They are also based on specific soil quality guidelines for the protection food safety and animal health from potential cadmium risk (MAF, 2011).

**Table A 5:** Hierarchy of documents containing soil guideline values<sup>a</sup> (MAF, 2011)

Endpoints	Reference documents	Source
<b>Human health only<sup>b</sup></b>	Health and Environmental Guidelines for Selected Timber Treatment Chemicals (MfE and MoH, 1997) Guidelines for Assessing and Managing Contaminated Gasworks Sites in New Zealand (MfE, 1997) Guidelines for Assessing and Managing Petroleum Hydrocarbon Contaminated Sites in New Zealand (MfE, 1999)	NZRB
	Guideline on the Investigation Levels for Soil and Groundwater (NEPC 1999) (health investigation levels, residential land use only). Assessment of Risks to Human Health from Land Contamination (DEFRA and EA, 2002) Soil Screening Guidance: Technical background document (US EPA, 1996a) and User's guide (US EPA, 1996b); Supplemental Guidance for Developing Soil Screening Levels at Superfund Sites (US EPA, 2001) Region 6 Human Health Medium- Specific Screening Levels (US EPA, 2002a) Region 9 Preliminary Remediation Goals (US EPA, 2002b)	IRB <sup>c</sup>

	Soil Guideline Values for cadmium in soil, Science Report SC050021 / Cadmium SGV (UK EPA, June 2009)  Supplementary information for the derivation of SGV for cadmium Better Regulation Science Programme Science report: SC050021/Technical review cadmium (UK EPA, June 2009)	
	Guideline on the Investigation Levels for Soil and Groundwater (NEPC, 1999) (all land uses except residential)	ITB
<b>Human health and ecological receptors</b>	Canadian Environmental Quality Guidelines (CCME, 2002)  Circular on Target Values and Intervention Values for Soil Remediation (Ministry of Housing, Spatial Planning and the Environment, 2000) <sup>d</sup>	IRB
<b>Ecological receptors only</b>	Ecological Soil Screening Level Guidance (US EPA, 2000)	IRB
	Guideline on the Investigation Levels for Soil and Groundwater (NEPC 1999) (ecological investigation levels)	ITB
<b>Groundwater</b>	Guidelines for Assessing and Managing Petroleum Hydrocarbon Contaminated Sites in New Zealand (MfE, 1999)	NZRB
	Soil Screening Guidance <sup>e</sup> (US EPA, 1996a and b)	IRB

NZRB = New Zealand risk-based; IRB = international risk-based; NZTB = New Zealand threshold based; ITB = international threshold based.

a No hierarchy is established for the documents within each category.

- b The underlying premise in existing New Zealand industry-based guidelines is that protection of on-site ecosystems is only required to the extent necessary to facilitate the use of the land (ie, plant growth and livestock). These guidelines have been classed as protecting human health only, as they do not consider the full extent of the protection of ecosystems as do the Canadian and Dutch documents.
- c UK, Canadian and Dutch criteria are the only criteria (other than New Zealand) that include produce consumption.
- d While Dutch criteria for human health protection are based on a residential land-use scenario, the majority of intervention values are based on protection of the ecosystem as these were lower than values derived for protection of human health. Hence, these values have a wider applicability than just to a residential land-use scenario.
- e US EPA Region 6 and Region 9 guidance documents also provide groundwater values. However, these values originate from US EPA, 1996a.